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Methods for Determining the Polychlorinated Biphenyl Emissions from Incineration and Capacitor and Transformer Filling Plants

Midwest Research Inst., Kansas City, Mo.

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METHODS FOR DETERMINING THE POLYCHLORINATED BIPHENYL EMISSIONS FROM INCINERATION AND CAPACITOR AND TRANSFORMER FILLING PLANTS

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16. ABSTRACT

Described are methods to measure the polychlorinated biphenyl (PCB) emissions from the stacks of municipal waste, industrial waste, and sewage sludge incinerators and from capacitor and transformer filling plants. The PCB emissions from the incineration plants are collected by impingement in water and adsorption on Florisil. The samples are extracted with hexane, concentrated through evaporation of the solvent, perchlorinated, and the polychlorinated biphenyl content measured as the decachlorinated isomer using a gas chromatograph equipped with a flame ionization detector. The PCB emissions from the capacitor and transformer filling plants are collected directly on Florisil, extracted with hexane and quantified against the appropriate Aroclor using a gas chromatograph.

The methods were developed from laboratory studies and field tested at nine incineration plants and two transformer filling plants.

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METHODS FOR DETERMINING THE TOTAL POLYCHLORINATED BIPHENYL EMISSIONS FROM INCINERATION AND CAPACITOR- AND TRANSFORMER-FILLING PLANTS

By

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EPA Contract No. 68-02-1780, Task 2

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Office of Research and Development
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Research Triangle Park
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FOREWORD

Midwest Research Institute under Task 2 of EPA Contract No. 68-02-1780 has developed sampling and analysis methods for PCB emissions from industrial, sewage sludge, and municipal refuse incinerators and from capacitor- and transformer-filling plants. The development and evaluation of these methods are described in this report.

Approved for:

MIDWEST RESEARCH INSTITUTE

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for L. J. Shannon, Director
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Sciences Division

August 23, 1977

PREFACE

In April 1976, the Quality Assurance Branch of EMSL, RTP, NC, was directed to develop and validate a method for measuring the PCB emissions from incinerators and from capacitor- and transformer-filling plants. From an extensive review of the available literature and from consideration of the various stack conditions that would be encountered, a tentative method was proposed and submitted to Midwest Research Institute for evaluation. The tentative method involved collecting the PCB's on a filter followed by a solid adsorbent and analyzing for PCB's by converting all PCB's collected to the decachlorobiphenyl (DCB) isomer.

Solid adsorbents were favored over the use of polyurethane foam for the following reasons: (1) low background; (2) simple cleanup procedure; (3) good quality control during manufacturing in relation to particle size, purity, density, etc., and (4) ready availability. The chromatographic grade adsorbent was preferred over the organic liquid for the following reasons: (1) no evaporation during sampling; (2) much less chance for contamination because the collector could be assembled in the laboratory, sealed, shipped to the site, placed in the sampling train removed at the completion of sampling, sealed, and then returned to the laboratory for sample recovery; (3) less hazardous to use than organic liquids; and (4) no loss of collection efficiency as water condensed in the impingers. The use of a filter was later deleted from the procedure because field studies under this contract and similar field studies done by others found negligible amounts of PCB's on the filters.

Perchlorination to convert all samples to the decachlorobiphenyl species was selected as the most effective means to accurately determine the PCB emissions from incineration sources because: (1) the electron capture detector response increases as the degree of chlorination increases; (2) only one standard is necessary for quantitation; (3) the "fingerprint" technique of quantitation, which involves relating the concentration of PCB to the nearest Aroclor, would not be applicable to incinerator-type sources, because different isomers might be destructed at different rates and because the refuse can contain many different polychlorinated biphenyls; and (4) the toxicity of the individual isomers is unknown so the intent of any regulation would likely be to minimize the total PCB emissions rather than the emissions of individual isomers.

William J. Mitchell
EPA Task Officer for Task
No. 2
EPA Contract No. 68-02-1780

ABSTRACT

A method for the sampling and analysis of PCB emissions from industrial, sewage sludge, and municipal refuse incinerators was developed from laboratory and field evaluations at nine incineration plants. The sampling method was based on modification of the Method 5 train, by removing the heated filter and adding a Florisil adsorbent tube, and sample recovery and PCB assay procedures were adapted from methods widely utilized for the analysis of PCB residues in environmental samples. The precision of the method, determined from field sampling in duplicate, was 13%.

The method was adapted for the determination of PCB emissions from capacitor- and transformer-filling plants. The sampling train was adapted by removing the ice-cooled impingers. The method was evaluated by sampling ambient air in impregnation rooms of two capacitor-filling plants. PCB concentrations as high as 2,500 $\mu g/m^3$ were determined with PCB breakthrough of < 0.15% (determined from a second Florisil tube connected in series). The PCB method is appended to this report.

This report is submitted in fulfillment of Task 2 of Contract No. 68-02-1780 by Midwest Research Institute under the sponsorship of the Environmental Protection Agency.

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Dr. William J. Mitchell, the EPA task officer for this project, is thanked for his guidance throughout the program and for his assistance in securing permission for sampling at five municipal incineration plants.

1.0 INTRODUCTION

The release of polychlorinated biphenyls (PCBs) into the environment has caused considerable concern because of their chronic toxicities, resistance to chemical and/or biochemical degradation, and their tendency to bioaccumulate in food chains (including man). The chemical stability and dielectric properties of PCBs have been utilized in a variety of applications. Prior to 1970, typical PCB uses were as plasticizers, heat transfer agents, as components of cutting oils and other special lubricants, as components of hydraulic fluids, in formulations of paints and other protective coatings, in adhesives, in carbonless reproducing paper, and as dielectric fluids in electrical capacitors and transformers. Following the identification of PCB residues in a variety of ecosystems, the Monsanto Company, sole producer of PCBs in the United States, restricted all PCB sales after 1972 to "closed system" uses, largely as dielectrics in capacitors and transformers. However, some PCBs and PCB-containing materials are still imported.

The diverse and considerable usage of PCBs during the middle of this century complicates the disposal of wastes containing these hazardous materials in a manner consistent with sound environmental management. Of the 1.4 billion pounds of PCBs sold in the United States since 1929, about 750 million pounds were exported, and about 500 million pounds have already entered the environment, mostly via landfills.[1/] The eventual disposal of the PCB-containing materials currently in service will likely result in their inclusion in industrial and municipal wastes. A part of these wastes are processed by incineration in industrial incinerators, municipal refuse incinerators, and sewage sludge incinerators.

Assessing the emission of PCB residues into the environment requires, in part, an evaluation of PCB emissions from these waste disposal facilities. This investigation was designed to develop appropriate sampling and analysis methods for determining PCB emissions from industrial, municipal refuse, and sewage sludge incinerators. A method was formulated so as to provide a standard reference method for PCB emissions from these stationary sources. In addition, the method was adapted for the measurement of emissions from capacitor- and transformer-filling plants, the current major users of PCB materials in the United States. This report describes the development and evaluation of the method. The method is appended to this report.

2.0 DEVELOPMENT OF THE PRELIMINARY PCB METHOD FOR INCINERATORS

2.1 Development of a Preliminary Sampling System

The design criteria for the development of the PCB sampling train included efficient, isokinetic collection of both vaporous and particulate-associated PCB residues (although not necessarily fractionated), from a variety of incinerator stack emissions (e.g., cool to hot gases, dry to supersaturated gases, etc.) in a form acceptable to the constraints of the analytical protocol to be developed. In addition, the simplicity of construction and operation and ruggedness under field sampling conditions were considerations.

A number of devices have been used to extract PCBs and/or chlorinated pesticides from ambient air and stationary sources. Many of these were reviewed by Margeson.[2] The most promising of these include polyurethane foam, the macroreticular resin Amberlite® XAD-2, Tenax®-GC, and Florisil. The foam and resin have also been applied to the extraction of the same compounds from waters. Although polyurethane foam has the attractive property of causing very little resistance to flow, cleaning the foam prior to use involves a lengthy series of extractions and blanks can be troublesome.

Although evaluated at low flows (2-3 liters/min) Florisil has been shown to be a very effective PCB adsorbent.[3] In addition, as silicate salt, Florisil is normally activated by heating to temperatures that destroy most organics so that very clean blanks may be achieved. XAD-2 has been utilized for the collection of a variety of organic species from air, including flue gases.[4] In particular, Amberlite® XAD-2 is the adsorbent used in the EPA Source Assessment Sampling System (SASS train). A stationary source sampling train incorporating Tenax®-GC has been developed and tested.[5] However, reports of *in situ* decomposition of Tenax during sampling may contribute to blank problems.[6]

2.1.1 Evaluation of adsorbents: Adsorbents selected for evaluation, Florisil® (60/100 mesh PR grade, Floridin Company), XAD-2® (20/50 mesh, Mallinckrodt, Inc.) and Tenax®-GC (35/60 mesh, Applied Sciences Laboratories, Inc.) were cleaned by overnight Soxhlet extraction with hexane and then dried overnight at 110°C. The Florisil was activated by heating to 650°C for 2 hr in a muffle furnace. Adsorbents were stored at 110°C until immediately prior to use.

Trapping efficiencies were determined by sampling laboratory air spiked with PCBs utilizing the sampling configuration shown in Figure 1. Small volumes (1-10 µl) of PCB standard solutions were deposited in the depression at the bottom of the sample introduction tube and were volatilized

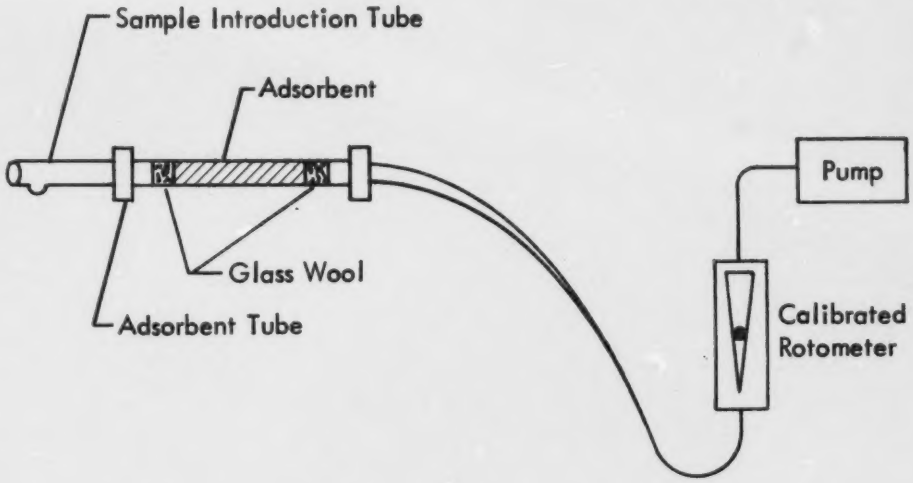

Figure 1 - Laboratory Sampling Train for the Evaluation of Adsorbents

into the airstream sampled by heating with a heat gun. Following sampling the source tube was removed and thoroughly rinsed with hexane. The adsorbent tube was eluted with 50 ml hexane. Both source and adsorbent tube extracts were concentrated to 5.0 ml in Kuderna-Danish evaporators and assayed by gas chromatography with electron capture detection (GC-EC) for the PCBs spiked into the sampling stream. The chromatographic column, 1.8 m x 2 mm ID glass packed with 3% OV-210 on 100/120 mesh Supelcoport®, was eluted with 30 ml/min of nitrogen. Injector and detector temperatures were 220 and 300°C, respectively. The column temperature was held isothermally at 165 to 200°C, depending on the particular PCB material assayed. Trapping efficiencies were calculated from the weight of PCB in the adsorbent extract compared to the weight spiked, corrected for the weight in the source tube extract.

For the preliminary trapping efficiency testing, the adsorbent tubes were ∿ 150 x 15 mm ID. The clean, dry adsorbent was weighed into the tubes, tared with a plug of cleaned glass wool in the exit end, and a second glass wool plug was added to contain the adsorbent. The volumes of adsorbents placed in the tubes were very similar; however, the weights were quite different because of density differences.

Test runs were completed with each of the three adsorbents with each of three PCB compounds at sampling rates of about 3.5 liters/min. Sampled air was spiked with 600 ng of 2,2'-dichlorobiphenyl (2CB), 600 ng of 2,4,2',5'-tetrachlorobiphenyl (4CB), or 700 ng of 2,3,4,2',3',4'-hexachlorobiphenyl (6CB). To get an indication of the restriction to flow caused by the adsorbent tubes, the flow rate was set at 4.0 to 4.1 liters/min before the tubes were fitted to the system. The 60/100 mesh Florisil provided the greatest restriction, reducing the flow rate by 31%; Tenax reduced the flow rate by 10%. The XAD-2 tube caused only slight flow rate reduction, ∿ 2%.

Tests were run for 10 min. The results of these tests are shown in Table 1.

TABLE 1

RESULTS OF ADSORBENT EVALUATIONS AT LOW SAMPLING RATES

	Adsorbent		
	Florisil	Tenax	XAD-2
Weight of adsorbent (g)	2.0	0.65	1.2
Sampling rate (liter/min)	2.8	3.7	4.0
Recovery (%)			
2CB	80.0	78.4	69.3
4CB	111	107	92.2
6CB	87.6	103	83.3

These results indicate that XAD-2 might be a less efficient PCB adsorbent.

A second series of tests was similarly completed at flow rates near 20 liters/min and with larger (22 mm ID) tubes to better simulate the sampling rates desired for isokinetic sampling. Flow restriction became a serious problem in the Florisil tests, where a sampling rate of 17 liters/min was the highest obtainable with the pumping system fitted to the train. The results of these tests are shown in Table 2.

TABLE 2

RESULTS OF ADSORPTION EVALUATIONS AT HIGH SAMPLING RATES

	Adsorbent		
	Florisil	Tenax	XAD-2
Weight of adsorbent (g)	6.5	2.4	6.0
Sampling rate (liter/min)	17	20	20
Recovery (%)			
2CB	71.4	82.7	34.0
4CB	90.5	92.8	59.2
6CB	80.6	91.0	57.0

Since the XAD-2 exhibited a much lower trapping efficiency for PCBs under these conditions, no further testing was conducted with this material.*

Although the trapping efficiencies for Florisil and Tenax appeared comparable and acceptable, the flow restriction of the Florisil could pose a serious problem when high sampling rates are required. A sample of 30/60 mesh Florisil, Grade A, was received from Floridin Company for evaluation to overcome the flow restriction problem. Since each batch of Florisil was routinely activated at 650°C, similar to the activation process used by Floridin Company to produce PR grade adsorbent, the activity of the treated 30/60 mesh A grade should be similar to that of the 60/100 mesh PR grade. A third series of trapping efficiency studies with the 30/60 mesh Florisil showed that the flow restriction was much less, similar to that experienced with the 35/60 mesh Tenax. Recoveries of 74.3, 89.7, and 111% for 2CB, 4CB, and 6CB, respectively, were found for 7.5 g of the coarser Florisil at a sampling rate of 20 liters/min.

* A specially prepared sample of XAD-2 was evaluted, however, as a part of the selected PCB sampling train. See Section 3.1.

In order to obtain information on the effects of higher gas stream temperatures and moisture content, two recovery studies were conducted with 2CB and 6CB. In the first study, the adsorbent tube was enclosed in a heated box held at 120°C. During the previous tests without the heated box, the adsorbent temperature was near 50°C from heating of the sampled air with the heat gun. In the second of these studies, two impingers were connected in series to the inlet of the sample introduction tube. The first impinger contained 100 ml of distilled water and the second was empty to trap entrained water. The results of these tests are shown in Table 3.

TABLE 3

RESULTS OF ADSORPTION EVALUATIONS AT ELEVATED TEMPERATURES AND MOISTURE IN SAMPLED GASES

	120°C		120°C + High Moisture	
	Tenax	Florisil	Tenax	Florisil
Weight of adsorbent (g)	1.5	5.0	1.5	5.0
Sampling rate (liter/min)	20	20	20	20
Recovery (%)				
2CB	I[a/]	68.6	I[a/]	58.6
6CB	53.4	49.9	44.3	50.9

a/ Severe interferences in the Tenax extract, 2CB, could not be quantified.

From these limited experiments, the trapping efficiencies for both adsorbents appear to be more affected by temperature of the adsorbent than the moisture content of the gas stream. Hence, an efficient sampling train design utilizing these adsorbents should allow for cooling of hot gases before introduction to the adsorbent.

In order to evaluate the trapping efficiencies of Florisil and Tenax adsorbent traps at run times that might by typical of those required in field sampling, a final series of recovery studies was conducted with run times of 10 min, 2 hr, and 4 hr at ambient laboratory temperature and moisture content. The results of these studies are shown in Table 4. Trapping efficiencies were decreased by long run times, but not markedly so.

TABLE 4

RESULTS OF ADSORPTION EVALUATIONS AT DIFFERENT RUN TIMES

		Florisil	Tenax
Weight of adsorbent (g)		7.5	2.0
Sampling rate (liter/min)		20	20
		2CB Recovery (%)	
Run Time:	10 min	59.4	62.4
	2 hr	47.9	40.4[a/]
	4 hr	47.0	49.5
		4CB Recovery (%)	
	10 min	99.7	85.9
	4 hr	82.2	79.4
	10 min	96.9	76.2
	2 hr		74.1
	4 hr	91.2	73.9

a/ Assay of Tenax extract is suspect; interfering peaks in chromatograms.

Although their trapping efficiencies were not as good as desired for the more volatile 2CB, Tenax and Florisil appeared to be roughly equivalent as PCB adsorbents. Increasing the temperature of the adsorbents had a much greater impact on their efficiencies than either the introduction of moderate levels of moisture or long run times.

2.1.2 Design and preliminary evaluation of candidate PCB sampling trains: Considering the PCB trapping evaluations of Florisil and Tenax, a PCB sampling train utilizing these adsorbents must provide for cooling the sampled gases (and likely condensation of water in saturated and supersaturated gases and removal of entrained droplets) prior to passage of the gases through the adsorbent trap. Several approaches to meeting these criteria were evaluated. In most cases, ice-cooled impingers were employed to cool and condense water from the sampled gases. One train design utilized a water-cooled condenser for this purpose. Heated and/or unheated filters were utilized to collect particulates or remove entrained water. The operating characteristics of candidate train designs were evaluated under field conditions by sampling at a sewage sludge incinerator of the Blue River municipal

sewage treatment facility in Kansas City, Missouri. The goal of these tests was to run at 20 liters/min for up to 4 hr. Since this evaluation was for operability only, the contents of the trains were not assayed for PCB residues.

Several operating principles were apparent. In most cases, the combination of one or more filters in series with the adsorbent tube generally caused excessive resistance to flow and in many cases did not allow operation at the desired flow rate. In addition, as particulates collected on filters, flow restriction increased dramatically. Two train designs, diagrammatically represented in Figure 2, exhibited acceptable operating characteristics. In the case of Train A, a Graham condenser and flask were utilized to cool the gases, condense and collect moisture. The condenser was modified with a glass extension tube to hinder entrainment of condensed water into the gas stream just in front of the adsorbent trap. A heated filter was placed in front of the condenser to trap particulates and simplify cleanup of the condenser following sampling. In Train B a series of three ice-cooled impingers similarly protect the adsorbent. Sampled gases were cooled and moisture condensed in the first two Greenburg-Smith impingers to which 100 ml of distilled water were added. The third impinger, a modified Greenburg-Smith type, was included to trap entrained water. To protect the pumping system the adsorbent tube was followed by two impingers. The first of these impingers held 100 ml of a 10% sodium hydroxide solution to neutralize acidic gases, such as the HCl that is produced in the incineration of chlorinated hydrocarbons, and the second had 300 g of silica gel to remove moisture.

The two train designs were further evaluated with both adsorbents by field testing at the Dade County (NE) municipal refuse incinerator in Miami, Florida. The same incinerator was also tested in evaluations described in Section 3.2.3. Paired Trains A and B with either Florisil or Tenax adsorbents were operated simultaneously for each sampling run. Since only limited testing was conducted, sufficient sampling equipment was prepared in the laboratory so that the trains could be disassembled and shipped back to the laboratory for sample recovery and analysis. In this manner the results of the evaluation were not biased by possible contamination during sample recovery in the field and field operations were simplified.

Upon receipt of the trains at the laboratory, sample recovery was initiated. The condensed water was batch extracted with three 100-ml portions of hexane. The filters from Train A were extracted with three 50-ml portions of hexane for 20 min each in a sonic bath. In order to determine the extraction requirements for the adsorbents used for field sampling, each trap was first eluted with 100 ml of hexane. The contents were then removed and Soxhlet extracted for 4 hr with 170 ml hexane and the extracts assayed separately. The requirements for rinsing the trains with organic solvents

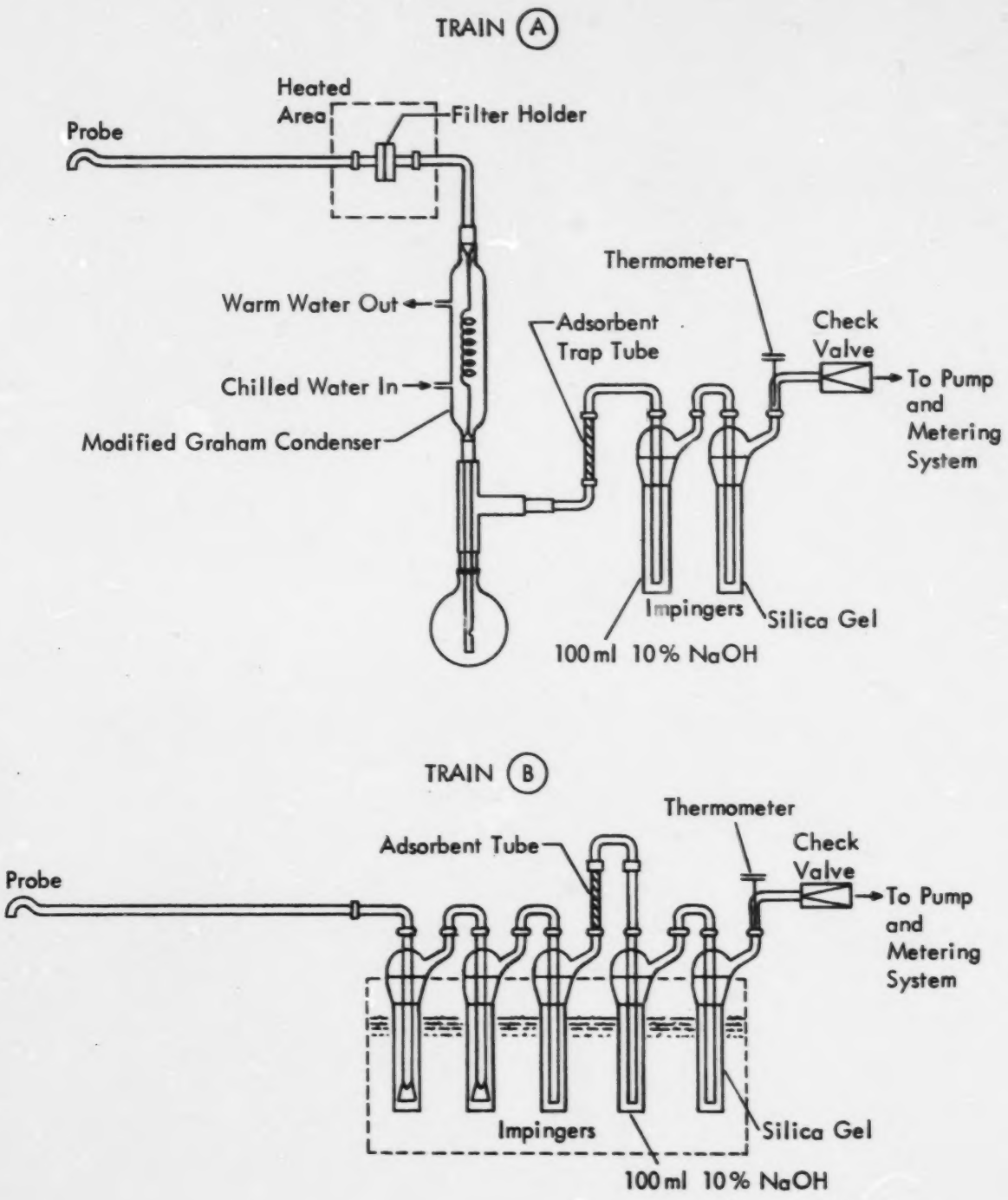

Figure 2 - Candidate PCB Sampling Trains

were investigated by rinsing the trains with distilled water (which was then extracted with hexane utilizing the same procedures as for condensed water) and then with a small amount of acetone, to remove moisture from the glass, prior to a thorough rinse with hexane. The extract of the aqueous rinses and the combined acetone and hexane rinses for each train were assayed separately.

All extracts were evaporated to ∿ 5 ml, dried by passage through a microcolumn (disposable pipette) of anhydrous sodium sulfate, and then cleaned up by shaking with 5 ml of concentrated sulfuric acid in vials with TFE®-lined screw caps. The PCB contents of the cleaned extracts were assayed by perchlorination of the PCBs to decachlorobiphenyl (DCB) by procedures described in Section 2.2 and then EC-GC analysis of the DCB. The chromatographic system described in Section 2.1.1 was utilized with the column temperature maintained at 240°C.

Table 5 summarizes the results of these evaluations. Since the sampling runs with the two adsorbents were conducted on different days, much of the variability in the amount of PCB materials recovered may be related to the variability of feed material and furnace conditions of the incinerator. Hence, direct comparison of the two adsorbents was not possible. Also, comparisons of the results from Trains A and B for a particular run are not conclusive. Nonetheless, from these and the previous evaluations, Florisil was selected as the best adsorbent alternative and Train B was selected as the best train design. In the laboratory evaluations, Florisil exhibited trapping efficiencies as good or better than those of Tenax. In addition, Florisil extracts exhibited consistently negligible levels of interfering co-extractants (likely resulting from the high activation temperature used on this inorganic adsorbent), compared to frequently troublesome blanks exhibited by Tenax extracts (as noted in Section 2.1.1). Although a minor consideration, Florisil is much less expensive than Tenax.

The selection of Train B as the best alternative offered several practical advantages. During the 4-hr test runs the pressure drop across Train A was ∿ 5.5 in. (140 mm) of Hg while the pressure drop across Train B was only ∿ 1 in. (25 mm) of Hg. In addition, the Train B design, essentially a Method 5 train modified by the removal of the heated filter and the addition of the adsorbent tube, is simpler and more compact to handle in the field and to maintain.

Examination of the PCB contents recovered from the components of the trains, Table 5, showed that simple elution of the adsorbent trap with an extracting solvent (although sufficient to extract PCB residues following laboratory evaluations) did not quantitatively extract PCB residues collected in source samples. Hence, the more rigorous Soxhlet extraction procedure must be used. In addition, rinsing of train components with hexane

TABLE 5

RESULTS OF PCB TRAIN EVALUATION TESTING AT DADE COUNTY (FLORIDA) MUNICIPAL REFUSE INCINERATOR

	Adsorbent			
	Florisil (30/60 mesh)		Tenax (30/60 mesh)	
Train[a]	A	B	A	B
Date sampled	7/14/76	7/14/76	7/15/76	7/15/76
Run number	1	1	2	2
Sampling rate (liter/min)	20	20	20	20
Sampling time (hr)	4	4	4	4
Weight of adsorbent (g)	7.5	7.5	2.0	2.0
Total PCB content (μg)				
Condensed moisture	22.8	10.4	0.72	3.25
Adsorbent (eluted)	9.90	4.55	6.25	3.80
Adsorbent (Soxhlet)	3.20	10.2	0.73	0.22
Filter	0.43	-	0.80	-
Probe rinse (water)	0.04	0.31	0.10	0.06
Probe rinse (hexane)	0.05	2.00	0.07	6.90[c]
Train rinse (water)	[b]	2.90	0.16	0.15
Train rinse (hexane)	12.70	6.10	1.30	1.30
Total	49.1	36.5	9.4	15.7

a/ Shown in Figure 2.
b/ This train was not rinsed with water.
c/ Possibly due to contamination.

is required to recovery PCB residues associated with the inner glass surface of the train. The acetone prerinse is necessary to remove water from the glass so that the water-immiscible hexane can effectively wet the surface.

2.2 Development of the Analytical Protocol

PCB residues have been assayed in a variety of environmental samples, often by procedures designed to determine chlorinated pesticides as well. The goal of the analytical development for PCB assays in stationary source emissions, specifically from incinerators, was to adapt the procedures generally employed for environmental samples and not to develop entirely new methods. Modifications of these procedures were designed to take advantage of the chemical stability of PCBs, by employing rigorous cleanup procedures inappropriate for pesticide/PCB assays, and to simplify quantification of "total" PCB residues, as in the utilization of perchlorination methods. Hence, a part of the analytical development described below involved verification of PCB recoveries from the various analytical techniques employed. More extensive evaluation of cleanup procedures and optimization of quantitation methods were also conducted.

2.2.1 Extraction procedures: Soxhlet extraction of PCB residues from the solid adsorbent and three-fold batch extraction from aqueous samples were employed for sample recovery. Quantitative recoveries were verified by the extraction of samples spiked with Aroclor 1221 and 1254. Soxhlet extractors were assembled with 170 ml of hexane and a plug of clean glass wool in the bottom of the sample holder. A 7.5 g portion of clean, activated Florisil (30/60 mesh) was added to the sample holder. The adsorbent was spiked with 10.5 μg Aroclor 1254 or 14.5 μg of Aroclor 1221 by injecting concentrated solutions (1.0 μg/μl) below the surface of the Florisil. Following extraction for 4 hr, the extracts were concentrated to 10.0 ml and assayed by EC-GC. The chromatographic system described in Section 2.1.1 was utilized with the column temperature held at 160°C for Aroclor 1221 assays and 210°C for Aroclor 1254 assays. Distilled water (200 ml) samples were similarly spiked in 1,000 ml separatory funnels. The spiked waters were batch extracted with three 100-ml portions of hexane, the combined extracts concentrated to 10.0 ml (Kuderna-Danish evaporators), dried by passage through a microcolumn of anhydrous sodium sulfate, and the PCB contents assayed by EC-GC. All extraction recoveries were run in triplicate.

The PCB contents of the recovered extracts were assayed by comparison with the Aroclors standards. Six major peaks in the elution pattern of Aroclor 1221 and seven major peaks for Aroclor 1254 (shown in Figure 3), were assayed individually. The total recoveries were calculated from the recoveries of the individual peaks. Hence both total recoveries and recoveries for several individual isomers (or groups of isomers where peaks represented coeluting PCBs) were determined.

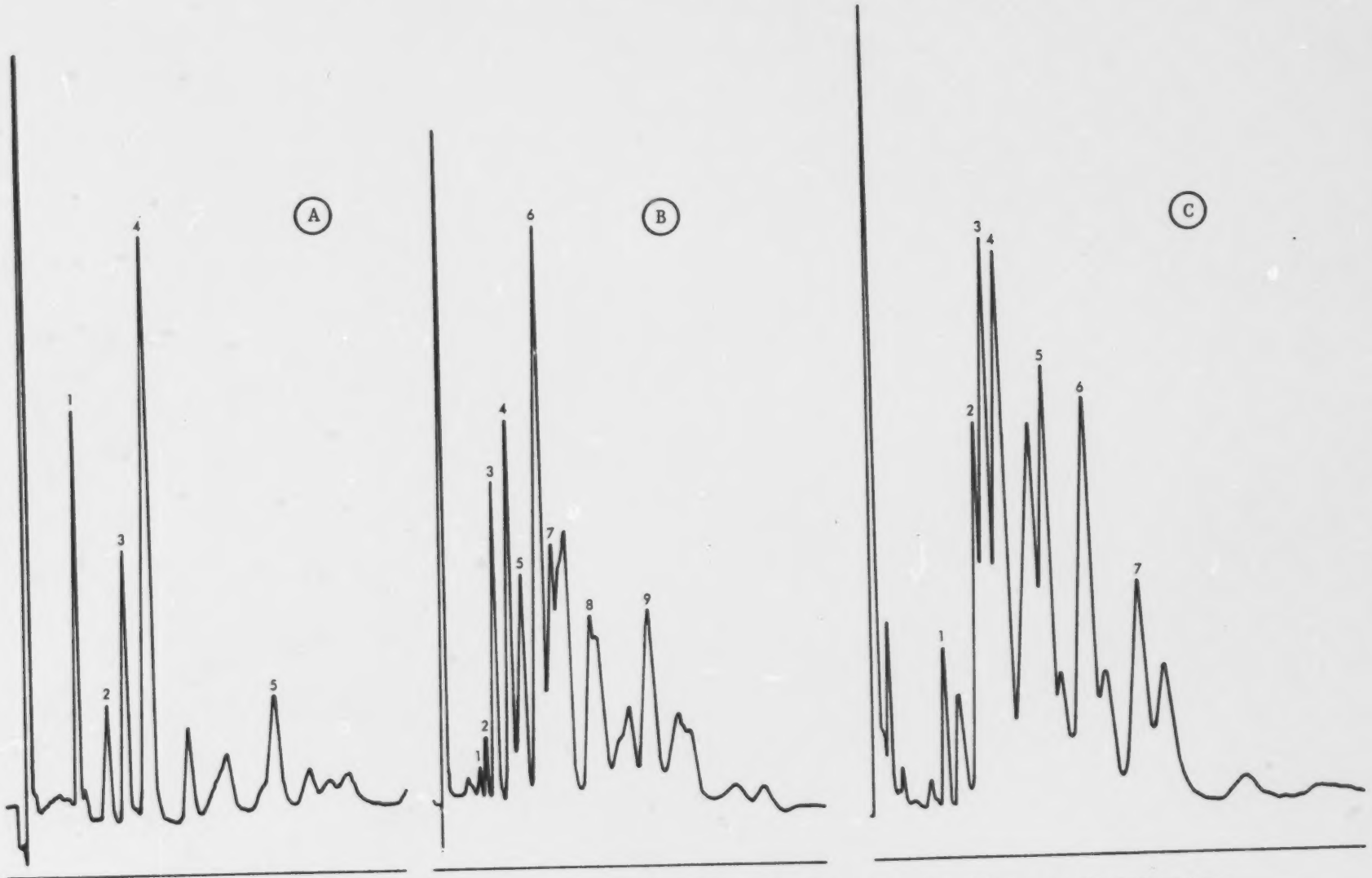

Figure 3 - Elution Patterns of Aroclor 1221 (A), 1242 (B), and 1254 (C) on an OV-210 Column Operated Isothermally at 160, 170 and 210°C, Respectively

The results of the extraction recovery studies are shown in Table 6. Recoveries were good but somewhat more variable in the case of Aroclor 1221. Part of this variability may be attributable to losses of more volatile compounds during extract concentration.

TABLE 6

RESULTS OF EXTRACTION RECOVERY STUDIES

PCB Mixture	Batch Extraction Recovery (%)	Soxhlet Extraction Recovery (%)
Aroclor 1221	76 ± 14[a/]	86 ± 10
Aroclor 1254	95 ± 8	91 ± 4

a/ Standard deviations are for recoveries of all peaks in all recovery tests.

2.2.2 Extract cleanup: The removal of interfering coextractants is an important part of PCB analytical protocols for environmental samples. In these studies, advantage was taken of the chemical stability of PCBs. Since PCBs are relatively resistant to sulfuric acid, which attacks many of the interfering materials, especially aromatics, PCB extracts in hexane were simply shaken with concentrated sulfuric acid. The hexane solution was then removed from the acid layer and the reacted interfering coextractants. Quantitative recovery of even the more acid-susceptible monochlorobiphenyls was demonstrated by spiking 5.0 ml portions of hexane with 2.5 µg each of o- and p-chlorobiphenyl, shaking for 1 min with 5 ml concentrated sulfuric acid in a vial with a TFE®-lined cap, and then assaying the chlorobiphenyls by EC-GC. The chromatographic system described in Section 2.1.1 was utilized with the column temperature held at 150°C. Recoveries averaged 107% for o-chlorobiphenyl and 105% for p-chlorobiphenyl for triplicate recovery determinations.

Although the sulfuric acid cleanup procedure is simple and allows good recovery of PCB residues, the coextracted material in some extracts may be acid-resistent or present in quantities too high to be removed efficiently. In these cases, the sulfuric acid cleanup can serve as a pretreatment for more extensive procedures such as adsorption chromatography on Florisil (60/100 mesh, PR grade). Florisil chromatography is a widely used technique for cleaning PCB and chlorinated hydrocarbon pesticide extracts for EC-GC assays and the procedures are described in the "Manual of Analytical Methods for the Analysis of Pesticide Residues in Human and Environmental Samples."[7/] Since these procedures have been verified and utilized by numerous investigators, no Florisil chromatographic development was included in the current

study. The recommended protocol for extract cleanup is to treat all extracts with sulfuric acid and further clean with the Florisil procedures where the nature and quantity of interfering coextractants require.

Some effort was devoted to the removal of biphenyl from the PCB residues. Biphenyl can form DCB during the perchlorination of PCB residues (as discussed in Section 2.2.3) and be included in total PCB assays. Although biphenyl is a significant component of commercial PCB mixtures with low chlorine contents, especially Aroclor 1221, its toxicity is much lower than chlorobiphenyls. In addition, biphenyl may be present in incinerator feed materials from sources other than PCB residues. Unfortunately, efforts to remove biphenyl from PCB residues were not successful.

Two widely used PCB and chlorinated pesticide cleanup techniques were evaluated for removing biphenyl: (1) fuming sulfuric acid/sulfuric acid/Celite column cleanup; and (2) acetonitrile/hexane partitioning. The procedures for both techniques were as described in the "Pesticide Analytical Manual"[8] except that hexane was substituted for petroleum ether and was used as the eluting solvent for the acid/Celite column. Aroclor 1254, Aroclor 1221, and biphenyl were all quantitatively (> 95%) recovered from standard solutions cleaned by acetonitrile/hexane partitioning. Aroclor 1254 and 1221 were spiked at 15.0 µg in their respective solutions and were assayed in the clean solutions by EC-GC methods described in Section 2.2.1. Biphenyl was spiked at 0.16 mg and was assayed in cleaned solutions by flame ionization GC (FID-GC) using the same chromatographic system but with the column operated at 120°C.

Standard solutions of these same materials were also cleaned by the fuming sulfuric acid/sulfuric acid/Celite procedure and assayed as described above. Biphenyl could not be detected in the cleaned solutions. Only 58.7% of the Aroclor 1221 passed the column and recoveries for the selected peaks of Aroclor 1221 ranged from 2.6 to 100% with only the later eluting peaks showing good recoveries. Aroclor 1254 was quantitatively recovered. Hence, biphenyl can be removed by this vigorous acid treatment, but only at the expense of losing significant quantities of the lower chlorinated biphenyls.

2.2.3 Quantitation: The complex composition of PCB residues in commercial PCB mixtures, environmental samples, and wastes complicates PCB quantitation. Often PCB residues are quantitated by comparison of EC-GC chromatograms with those of a commercial Aroclor mixture that is most similar. To improve comparisons the areas or heights of selected major peaks common to the residues and the Aroclor are summed. These procedures work well with very clean extracts where the residue closely resembles that Aroclor. Difficulties arise in these peak summation or "fingerprinting" techniques when the residue does not closely resemble the particular Aroclor

used for quantification or if interfering materials produce peaks that coelute with the selected PCB peaks.

Chemical and/or biochemical processes can alter the composition of PCB residues and residues may not be derived from a single commercial PCB product. As an example, tetrachlorobiphenyls and hexachlorobiphenyls appear to be the major contributors to PCB residues in Great Lakes fish,[9] a composition unlike any specific Aroclor. Some methods have addressed this problem by attempting to quantify parts of PCB residues against more than one Aroclor for different portions of the chromatogram. However, these procedures may become both complex and subjective.

PCB residues may be quantified by GC employing electrolytic conductivity detectors to gain increased specificity over electron capture detection. However, problems of sorting out the composition of the residue can still cause serious complications.

GC/MS techniques may offer the most unambiguous quantitative and qualitative characterization of PCB residues. Operating in the selected ion monitoring (SIM-GC/MS) mode, chromatograms of the ion intensities of ions characteristic of PCB isomers may be obtained with sensitivities rivaling EC-GC. From the ion chromatograms of two or more ions characteristics of biphenyls with a specific number of chlorine substitutions, non-PCB interferences can be sorted out and that part of the residue quantified with the aid of a computer.[10] Unfortunately, the equipment and technological investments required for these techniques is beyond that available to many laboratories.

To meet the requirement of the current study for a simple total PCB assay, results may be achieved more easily by chemical conversion of the PCB residues to decachlorobiphenyl (DCB) and then assaying the DCB. Although qualitative information on the composition of the PCB residues is lost, the residue is composited into a single compound with 10 chlorines, and more sensitivity to electron capture detection. In addition, the vigorous perchlorination reaction often destroys some residual coextractants.

Exhaustive chlorination techniques for PCBs were reported by Berg et al.,[11] refined by Armour[12] and Huckins et al.,[13] and have been utilized for PCB assays in a variety of environmental extracts. Similar procedures have also been applied to a mixture of other chlorinated aromatics.[14] Veith[15] and Haile and Armstrong[16] reported good correlation between assays of fish extracts by perchlorination and peak summation techniques.

Some interferences to the perchlorination procedures have been reported. Trotter and Young[17] found significant quantities of DCB in extracts of several antimony pentachloride reagents. However, in the current study and

several previous investigations, this author has not encountered reagent blanks containing more than a few nanograms per reaction. In a recent investigation of coal extracts and gaseous emission samples (collected on Tenax) from a coal-fired utility boiler plant, Haile[18] found several extracts that produced DCB during perchlorination in which PCB residues could not be confirmed by SIM-GC/MS. It was concluded that the extracts contained large quantities of biphenyl and/or related aromatic compounds that perchlorinated to DCB and that GC/MS identification was necessary for verification of PCB residues. Samples from incinerators, specifically designed to destroy the feed material, should be much cleaner than coal extracts or emissions from coal-fired boilers so that perchlorination techniques for PCB analysis should be more applicable. Nonetheless, the necessity for efficient cleanup of extracts and PCB verification by GC/MS should not be neglected.

The basic procedure utilized in this study, adapted by Veith[15] from the Armour[12] method, involved evaporation of the cleaned extract just to dryness in a small (∿ 5-ml) culture tube. An excess of antimony pentachloride (0.2 ml) was added and the tubes heated to 180°C for 4 hr. The reaction was quenched by cooling to ambient temperature and adding 2 ml of 6 N HCl. DCB was extracted with four ∿ 1-ml portions of hexane, dried by passage through a microcolumn (disposable pipette) of anhydrous sodium sulfate, and then assayed by EC-GC. Under these conditions good conversion (85-100%) of Aroclor mixtures to DCB have been observed; however, conversions of mono- and dichlorobiphenyls are much less and DCB yields from biphenyl are negligible.[18]

The development of perchlorination techniques in this study was devoted to optimizing the reaction conditions to achieve good conversion of the lower chlorinated biphenyls. Reaction times from 1 to 4 hr and temperatures from 140 to 175°C were evaluated by perchlorinating solutions of single chlorobiphenyl isomers. Triplicate reactions were conducted with 31 μg of 2,2'-dichlorobiphenyl (2CB), 22.5 μg of 2,5,2'-trichlorobiphenyl (3CB), 22.7 μg of 2,5,2',4'-tetrachlorobiphenyl (4CB), and 28.7 μg of 2,3,4,5,6,2',5'-heptachlorobiphenyl (7CB). Percent yields were calculated from the DCB assays compared to the theoretical molar yields. The results of these evaluations are shown in Table 7. From these results, reaction at 160°C for 2 hr was selected as providing the best combination of yields for these chlorobiphenyls. Conversion efficiencies were also determined for Aroclor 1221, Aroclor 1254, monochlorobiphenyls, and biphenyl using these conditions. The result of evaluations (six replicates) for perchlorination under the selected reaction conditions are summarized in Table 8. Reagent blanks for the perchlorination reaction averaged 6 ng. The only two of the 18 blanks ran that exceeded 10 ng were 25 and 38 ng.

TABLE 7

YIELDS OF DCB FROM SELECTED CHLOROBIPHENYLS BY PERCHLORINATION UNDER DIFFERENT REACTION CONDITIONS

Reaction Temperature (°C)	Reaction Time (hr)	Yields of DCB (%) from 2CB	3CB	4CB	7CB
140	2	80.0	96.5	101	110
150	2	75.0	84.6	83.8	102
160	2	89.2	96.3	89.5	100
175	1	95.1	88.0	101	88.9
175	2	64.1	74.0	84.2	82.0
175	3	62.0	85.3	76.2	86.6
175	4	75.7	72.2	86.0	82.0

TABLE 8

PERCENT YIELDS OF DCB FROM CHLOROBIPHENYLS BY PERCHLORINATION AT 160°C FOR 2 HR

Chlorobiphenyl	Weight Added (µg)	Yield of DCB (%)
Biphenyl	4.9	61.2
o-1CB	5.0	76.8
p-1CB	5.0	42.5
2CB	31.0	89.2
3CB	22.5	96.3
4CB	22.7	89.5
7CB	28.7	100
Aroclor 1221	0.64	80.2
Aroclor 1242	1.0	84.1
Aroclor 1254	0.58	82.1

Since the lower chlorinated biphenyls generally exhibited lower DCB yields from perchlorination, the possible loss of these more volatile PCBs during evaporation of the extracts was investigated. Aliquots of hexane (5 ml) in the culture tubes were spiked with 5 µg of each monochlorobiphenyl, evaporated just to dryness with a gentle stream of dry nitrogen, redissolved in 5.0 ml of hexane, and assayed by EC-GC. Recoveries following evaporation were 84.8 and 81.5% for the ortho and para isomers, respectively. Hence losses from evaporation likely contribute to the lower DCB yields of monochlorobiphenyls, but not markedly so.

Some investigators have reported good DCB yields by slowly heating the reaction mixture to temperature and allowing the reaction to continue overnight. Limited exploration of this procedure with Aroclor 1221 and 1254 standards resulted in yields of 76.1 and 76.8%, respectively, for the two Aroclors. These yields are 4 to 5% less than obtained from 2-hr reactions.

3.0 EVALUATION OF THE PCB METHOD FOR INCINERATORS

3.1 Laboratory Evaluation of Sampling Train Efficiency

The selected sampling system was subjected to extensive laboratory evaluation to determine collection efficiency. Sampling trains were assembled and operated in the laboratory by procedures similar to those used in field sampling. After the trains were leak checked, without a probe, sample introduction tubes, similar to that described in Section 2.1.1, were attached. Sampling tests were run at a flow rate of 20 liters/min for 4 hr. During each 30 min period of the tests, an aliquot (10-25 μl) of an Aroclor standard solution (Aroclor 1221, 1242, or 1254) in hexane was added to the depression in the sample introduction tube. The PCB spikes were volatilized into the sample stream with a heat gun. After completion of the test runs, the trains were disassembled and the sample recovered according to the preliminary method. The adsorbent tubes and impinger contents were extracted, train rinsings were added to the impinger extracts, and the extracts concentrated. Extracts were not cleaned up but were assayed directly by EC-GC comparison with the appropriate Aroclor by procedures described in Section 2.2.1. Six major peaks in the elution pattern of Aroclor 1221, nine major peaks for Aroclor 1242, and seven major peaks for Aroclor 1254 (see Figure 3) were selected for quantification. The results of these tests are shown in Table 9.

The distribution of the PCBs in the impinger and adsorbent sections of the trains was quite interesting. The earlier eluting, and likely more volatile, PCB compounds were generally recovered from the Florisil adsorbent (evidently easily passing through the series of impingers), while the later eluting PCBs were more likely to be recovered from the impingers. Typically all of the Aroclor 1221 and nearly all of the Aroclor 1242 was recovered from the Florisil. The seven peaks of Aroclor 1254 were generally distributed in both portions of the train. Table 10 shows the distribution from a typical test run.

Although XAD-2 had been abandoned as an adsorbent alternative in the preliminary tests (Section 2.1.1), a specially prepared sample (received from Dr. Phillip Levins, A. D. Little, Inc.) was evaluated as a part of the selected PCB train. The resin had been prepared by an extensive series of exhaustive Soxhlet extractions with water, methanol, diethyl ether, and pentane.[4] A train with 5.7 g XAD-2 tube recovered 88% of the spiked Aroclor 1221 when evaluated as described above. However, because of the rather involved resin preparation required, Florisil was retained as the selected adsorbent.

TABLE 9

SAMPLING EFFICIENCY OF PCB SAMPLING TRAIN

PCB Mixture	Total Spike (µg)	Recovery[a/] (%)
Aroclor 1221	23.8	86 ± 9
Aroclor 1242	18.2	88 ± 10
Aroclor 1254	11.6	92 ± 3

a/ Average and standard deviation for six tests.

TABLE 10

DISTRIBUTION OF AROCLOR 1254 SPIKE IN THE SAMPLING TRAIN

Peak No.	Recovery in Impingers (%)	Recovery in Adsorbent (%)	Total Recovery (%)
1	22.9	75.2	98.1
2	32.3	57.8	90.1
3	39.7	50.6	90.3
4	63.5	31.1	94.6
5	77.3	21.6	98.9
6	82.6	14.3	96.9
7	81.1	11.1	92.9
Mean			94.4

3.2 Field Evaluations

The PCB sampling and analysis method was also evaluated by testing at two municipal sewage sludge incinerators, two industrial incinerators, and five municipal refuse incinerators. In all tests, two identical trains were operated simultaneously to aid evaluation of the precision of the method. The PCB results of all tests are expressed as DCB and were not corrected for perchlorination efficiency.

3.2.1 Municipal sewage sludge incinerators: Emissions were sampled from sewage sludge incinerators at municipal sewage treatment facilities in the Kansas City, Missouri area. The Blue River facility of the City of Kansas City, Missouri, receives wastes with a significant industrial component while the facility of the City of Mission, Kansas, receives mostly domestic wastes. Sludges are dewatered by vacuum filtration in both plants prior to incineration. Both incinerators operate under induced draft and employ a wet scrubber for air pollution control. The Mission, Kansas, incinerator is diagrammatically represented in Figure 4.

Table 11 summarizes the test data and PCB results for testing of outlet flue gases for both incinerators. Extracts of all samples from the incinerators required cleanup by chromatography on Florisil in addition to sulfuric acid cleanup to remove interfering coextractants. The Blue River samples contained much higher levels of PCBs.

3.2.2 Industrial incinerators: Two incineration plants, designed and operated for contract incineration of industrial wastes, were sampled during staged test burns of PCB-containing wastes. The two incinerators were designed and operated quite differently. The Rollins Environmental Services facility in Deer Park, Texas, diagrammatically represented in Figure 5, burns, solid wastes and is primarily fired with petroleum-based fuels. Wastes are conveyed into a rotary ignition chamber. The plant employs an afterburner and a wet scrubber to achieve high efficiency combustion and control emissions. During the first day of testing ground capacitors, containing ~17% PCB fluids, were combusted. Whole capacitors were burned during the second day of testing.

The second industrial incinerator, to be identified only as Plant B herein, handles liquid wastes and is fired with the wastes only. The composition of the wastes, largely petroleum-based solvents, was adjusted to optimize incineration. During tests, liquid wastes containing approximately 10% PCB fluids, estimated by the plant operators, were incinerated. Emissions control was with a packed-tower scrubber.

The results of these tests are summarized in Table 12. Only three samples were collected at the Rollins incinerator. Samples 1A and 1B were taken during the burn of ground capacitors and 2A was collected during the burn of whole capacitors. Unfortunately, excessive breakage of train components in shipping prevented assembly and sampling to duplicate the 2A sample.

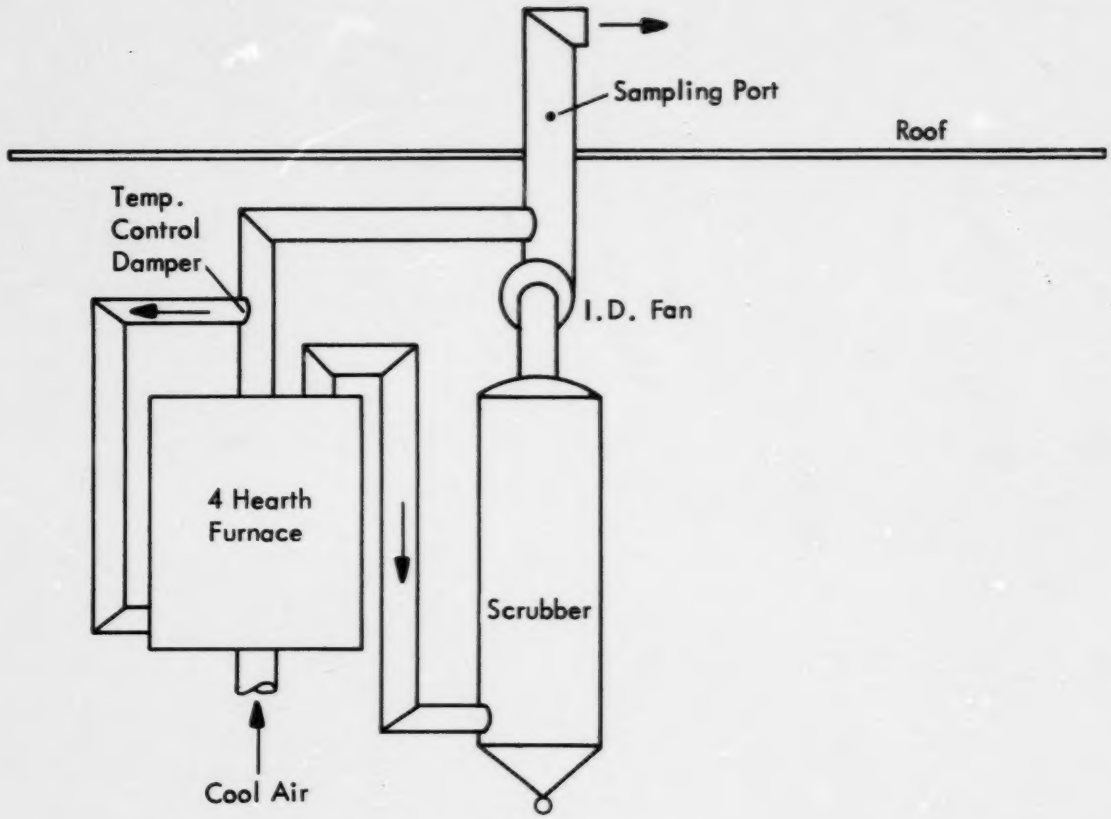

Figure 4 - Schematic Illustration of the Mission, Kansas Sewage Sludge Incinerator

TABLE 11

SUMMARY OF PCB RESULTS (AS DCB) FOR TWO SEWAGE SLUDGE INCINERATORS

Incinerator	Blue River (Kansas City), MO				Mission, KS	
Run Number	1	2	3	4	1A	1B
Date	10/11/76	10/11/76	10/11/76	10/11/76	4/12/76	4/12/76
Sampling Location	Outlet	Outlet	Outlet	Outlet	Outlet	Outlet
Volume of gas sampled (dscf)[a/]	118.4	95.6	82.8	83.8	104.0	99.7
Volume of gas sampled (dscm)[a/]	3.35	2.71	2.35	2.37	2.95	2.82
Percent moisture	15.8	17.3	13.6	13.0	11.1	8.8
Flue gas temperature (°F)	[b/]	[b/]	[b/]	[b/]	140	140
Feed rate (lb/hr)	--	--	--	--	1463	1463
Total PCBs in sample (μg, as DCB)	1022	836	674	233	11.3	10.6
PCB concentration in sample (10^{-6} grains/dscf, as DCB)	133	135	126	42.9	1.7	1.6
PCB concentration in sample (μg/dscm, as DCB)	305	308	287	98	3.80	3.70
Average PCB concentration in sample (μg/dscm, as DCB)	306		192		3.75	

a/ dscf = dry standard cubic foot
dscm = dry standard cubic meter

b/ Not recorded

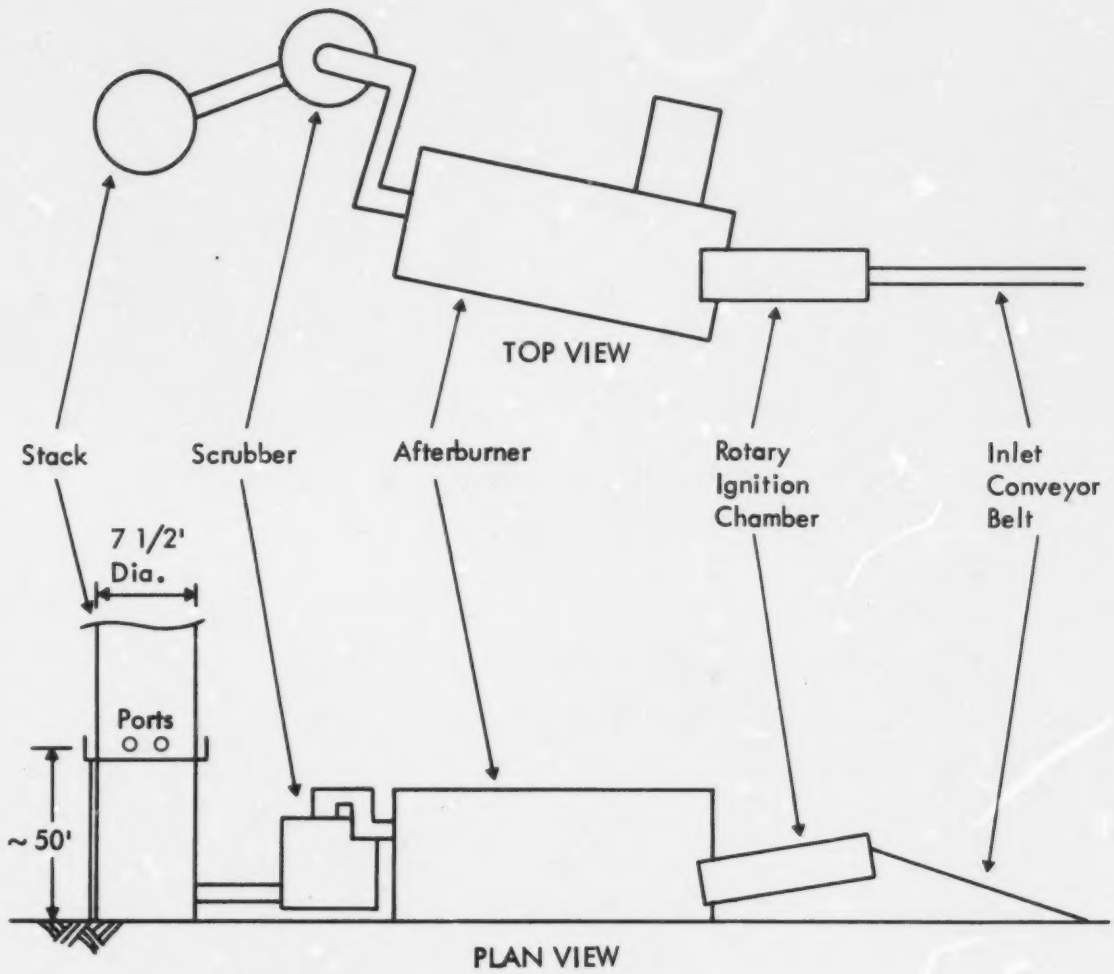

Figure 5 - Schematic Illustration of the Rollins, Inc., Industrial Incinerator, Deer Park, Texas

TABLE 12

SUMMARY OF PCB RESULTS (AS, DCB) FOR TWO INDUSTRIAL INCINERATORS

Incinerator	Rollins, Inc. (Deer Park, TX)			Industrial Incinerator B			
Run Number	1A	1B	2A[a]	1A	1B	2A	2B
Date	12/8/76	12/8/76	12/9/76	3/15/66	3/15/77	3/16/77	3/16/77
Sampling Location	Outlet	Outlet	Outlet	Outlet	Outlet	Outlet	Outlet
Volume of gas sampled (dscf)[b]	62.33	61.52	75.40	117.7	24.3	134.3	137.17
Volume of gas sampled (dscm)[b]	1.76	1.74	2.13	3.33	0.69	3.80	3.88
Percent moisture	34.1	33.3	35.2	14.0	1.9[c]	1.8[c]	2.3[c]
Flue gas temperature (°F)	130	130	130	122	122	147	147
Feed rate (gal/hr)	--	--	--	450	450	450	450
Total PCBs in sample (µg as DCB)	1.42×10^{-3}	1.18×10^{-3}	3.9×10^{-3}	0.789	0.283	0.226	0.349
PCB concentration in sample (10^{-6} grains/dscf, as DCB)	0.35	0.30	0.80	103	180	26.0	39.3
PCB concentration in sample (µg/dscm, as DCB)	0.79×10^{-3}	0.69×10^{-3}	1.83×10^{-3}	237×10^{-3}	410×10^{-3}	59.0×10^{-3}	90.0×10^{-3}
Average PCB concentration in sample (µg/dscm, as DCB)	0.74×10^{-3}			324×10^{-3}		74.5×10^{-3}	

a/ Run 2B was disabled by breakage

b/ dscf = dry standard cubic foot
dscm = dry standard cubic meter

c/ Percents of moisture for these runs are questionable

Although the moisture content of flue gases from the Rollins plant was high, the test burns only allow sampling for less than 2 hr and water accumulation in the impingers was not excessive.

Sample extracts from these incinerators were rather clean so that sulfuric acid treatment was sufficient to remove interfering materials. The efficiencies of these incinerators was demonstrated by the lowest PCB concentrations sampled.

3.2.3 Municipal refuse incinerators: Five municipal refuse incinerators in the Miami-Ft. Lauderdale (FL) area were sampled for PCB emissions for purposes of method evaluations. Both inlet and outlet samples were collected at three incinerators.

Outlet samples were collected from the Miami incinerator No. 1, diagrammatically represented in Figure 6. The incinerator was operated under induced draft and utilized a water sprayer for pollution control. Municipal refuse is fed in a batch mode.

The Dade Co., N.E. incinerator was tested during evaluations of preliminary train designs, described in Section 2.1.2. A schematic illustration of the incinerator, which operates under induced draft, is shown in Figure 7. Flue gas samples were collected after the electrostatic precipitator.

Both inlet and outlet samples were collected from the No. 1 (South Side) and No. 2 incinerators at the Broward Co. Plant No. 1 in Ft. Lauderdale. Incinerator No. 2 operates in the batch mode. Both incinerators operate with induced draft and utilize scrubbers for pollution control. The design of Incinerator No. 1 is shown in Figure 8. Figures 9 and 10 show the design of Incinerator No. 2 and the location of inlet and outlet sampling points, respectively. Inlet and outlet samples were also collected from the Broward Co. Plant No. 2, Incinerator No. 4, in Pompano Beach. This incinerator is diagrammatically represented in Figure 11.

The results of the method evaluation testing at municipal refuse incinerators are summarized in Table 13. The method was modified for inlet sampling by using a water-cooled stainless steel probe to withstand the high flue gas temperatures of these samples. During two of the runs at the Broward Co. Plant No. 1, Incinerator No. 1, the impingers filled with condensed water such that it splashed onto the Florisil. In these cases the runs were terminated because of the excessive pressure drops across the trains. Subsequent sampling at Incinerator No. 2 and Plant No. 2, Incinerator No. 4 was conducted with two additional empty impingers connected in series just in front of the adsorbent tube to collect water. Part A of the proposed method was appended to accommodate this special case.

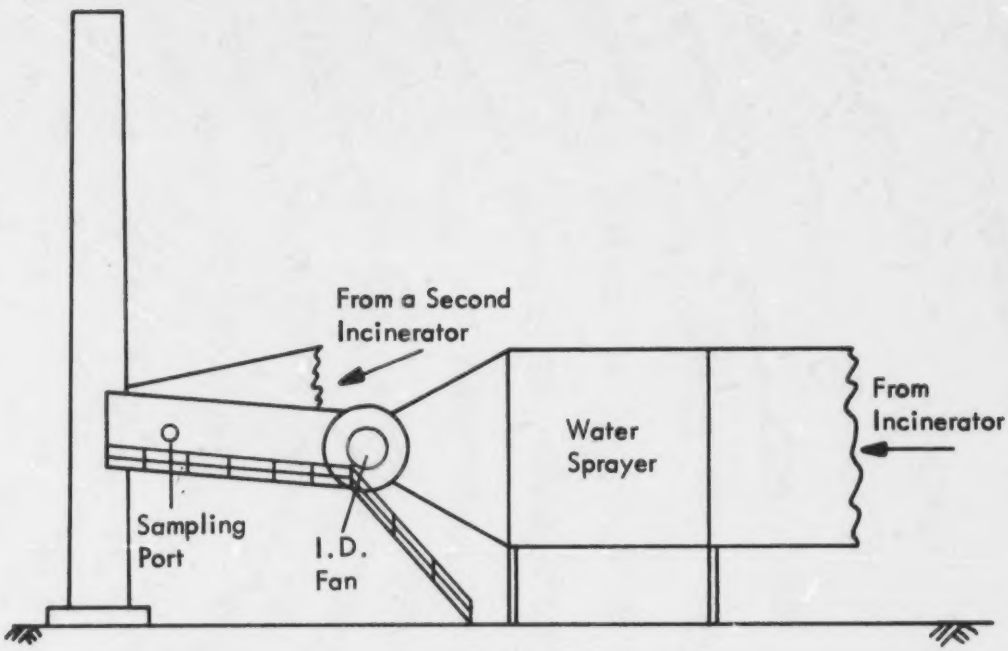

Figure 6 - Schematic Illustration of the Miami (FL) No. 1 Municipal Incinerator

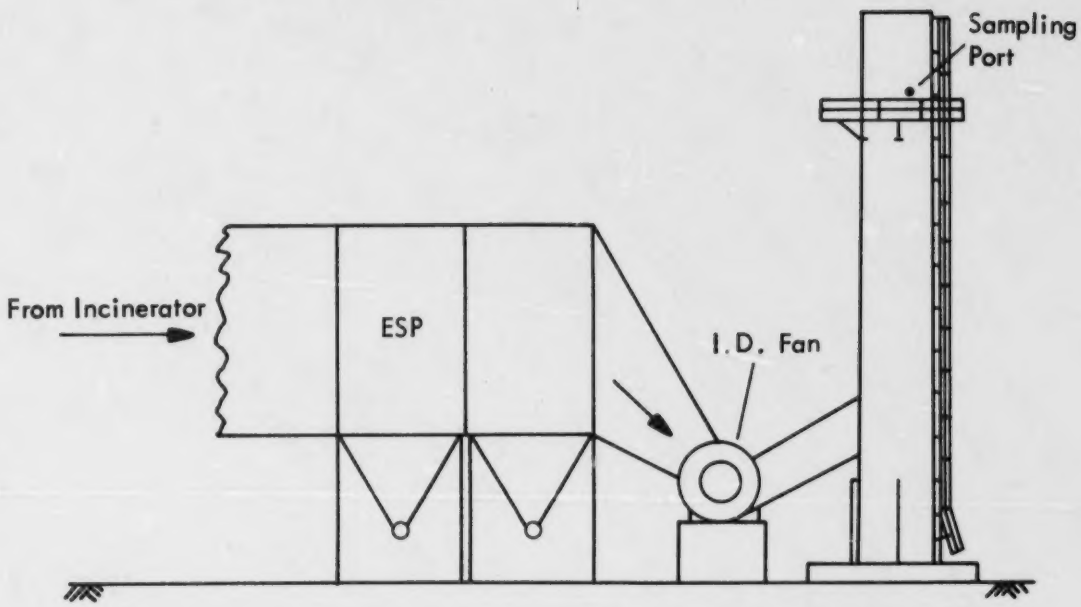

Figure 7 - Schematic Illustration of Dade Co. (FL), N.E. Municipal Incinerator

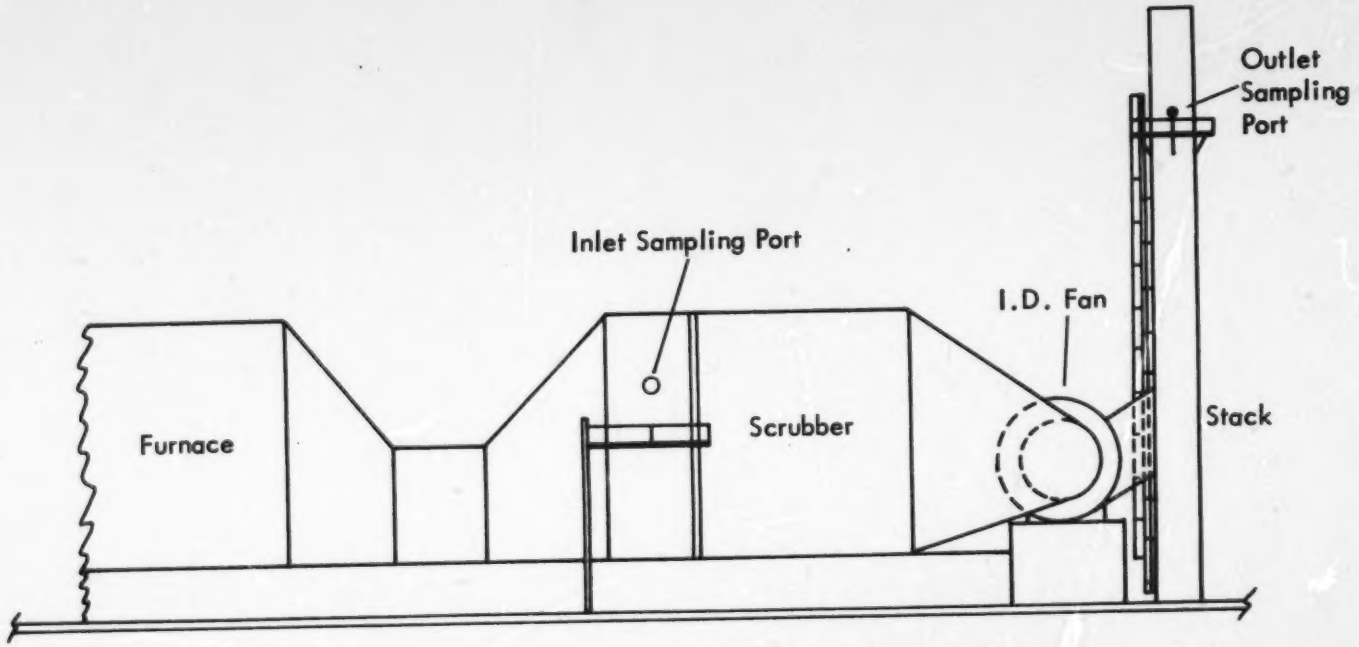

Figure 8 - Schematic Illustration of Broward Co. Plant No. 1,
Ft. Lauderdale, Florida, Incinerator No. 1
(South Side)

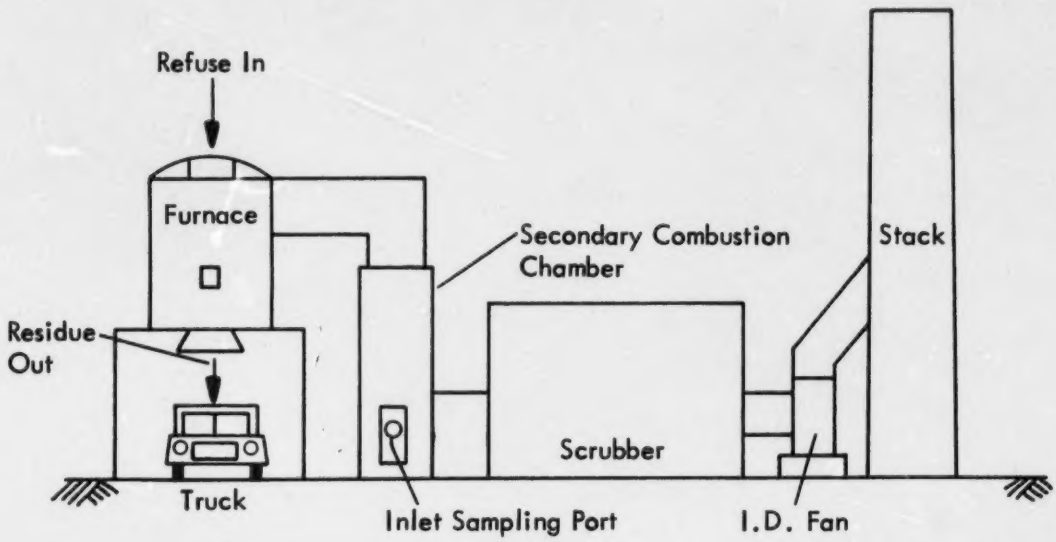

Figure 9 - Schematic Illustration of Broward Co. Plant No. 1, Ft. Lauderdale, Florida, Incinerator No. 2 (Batch), Inlet

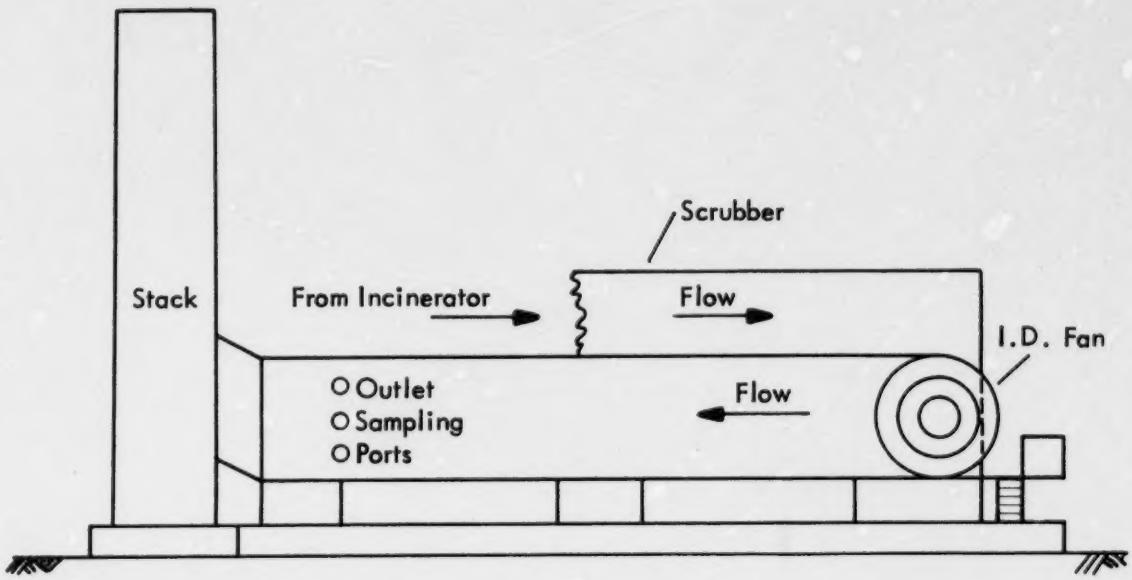

Figure 10 - Schematic Illustration of Broward Co. Plant No. 1, Ft. Lauderdale, Florida, Incinerator No. 2 (Batch), Outlet

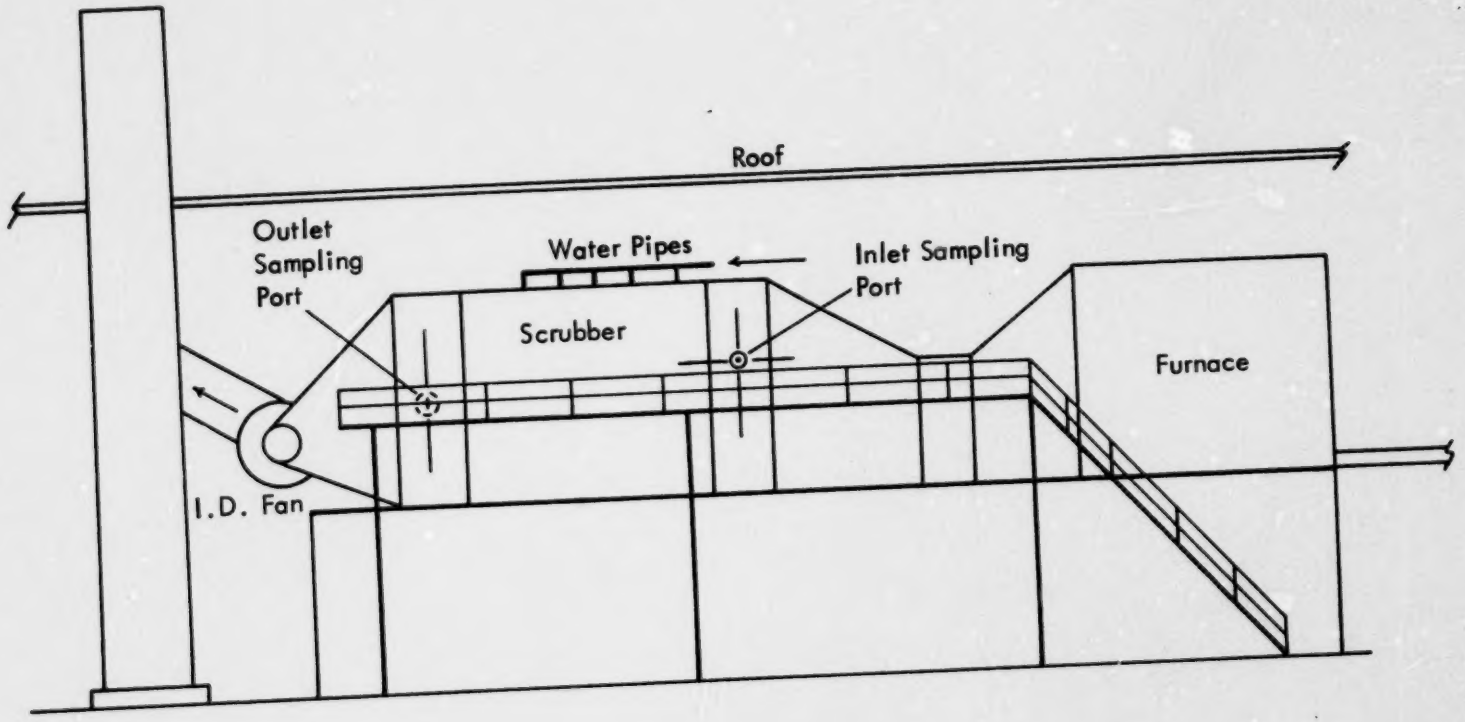

Figure 11 - Broward Co. Plant No. 2, Pompano Beach, Florida,
Incinerator No. 4

TABLE 13

SUMMARY OF PCB RESULTS (AS DCB) FOR FIVE MUNICIPAL REFUSE INCINERATORS

Incinerator	Miami (FL) No. 1 (Batch)		Dade Co. (FL), NE		Broward Co. (FL) Plant No. 1, Ft. Lauderdale								Broward Co. (FL) Plant No. 2 Pompano Beach No. 4			
					No. 1 South Side				No. 2 (Batch)							
Run Number	1A	1B	2A	2B	3A1	3B1	3A1	3B1	3A2	3B2	3A2	3B2	4A	4B	4A	4B
Date	1/18/77	1/18/77	1/19/77	1/19/77	1/21/77	1/21/77	1/21/77	1/21/77	1/24/77	1/24/77	1/24/77	1/24/77	1/25/77	1/25/77	1/25/77	1/25/77
Sampling Location	Outlet	Outlet	Outlet	Outlet	Inlet	Inlet	Outlet	Outlet	Inlet	Inlet	Outlet	Outlet	Inlet	Inlet	Outlet	Outlet
Volume of gas sampled (dscf)[a/]	92.95	91.49	86.44	83.38	46.01	44.81	132.7	138.7	60.74	68.19	82.08	79.17	62.20	65.80	122.0	125.7
Volume of gas sampled (dscm)[a/]	2.63	2.59	2.45	2.36	1.30	1.27	3.76	3.93	1.72	1.93	2.32	2.24	1.76	1.86	3.45	3.56
Percent moisture[b/]	9.6	9.6	13.4	8.9	20.3	21.0	29.2	14.8	3.2	14.2	20.5	19.6	2.5	13.1	18.5	15.5
Flue gas temperature (°F)	300	300	460	460	1800	1800	155	155	1400	1400	135		540	540	430	430
Feed Rate (ton/hr)	12	12	12	12	9	9	9	9	5	5	5	5	6	6	6	6
Total PCBs in sample (μg, as DCB)	93.8	83.5	34.1	15.5	15.6	19.2	8.40	8.40	8.97	6.22[c/]	9.48	15.7	16.5	10.4	10.2	14.2
PCB concentration in sample (10^{-6} grains/dscf, as DCB)	15.5	14.0	6.1	2.9	5.2	6.6	1.0	0.9	2.3		1.8	3.0	4.1	2.4	1.3	1.7
PCB concentration in sample (μg/dscm, as DCB)	35.5	32.0	13.9	6.6	11.9	15.1	2.3	2.0	5.3		4.1	6.9	9.4	5.5	3.0	3.9
Average PCB concentration in sample (μg/dscm, as DCB)	33.8		10.3		13.5		2.2		5.3		5.5		7.5		3.5	

a/ dscf = dry standard cubic foot
dscm = dry standard cubic meter

b/ Flue gases of runs 3A1 outlet, 3A2 outlet, and 3B2 outlet were supersaturated with water. Moisture contents of runs 3B1 outlet, 3A2 inlet, and 5A inlet are questionable and were not considered in subsequent calculations.

c/ The impinge extract was lost for this run so the results were not averaged.

Sample extracts from all municipal refuse incinerators required the additional cleanup of the Florisil chromatography procedure. The impinger extract of sample 3B2 outlet was lost so that the assay for this sample reflects only the contents of the adsorbent tube.

3.2.4 Results of field evaluations: In the course of the field evaluations, samples were collected from supersaturated flue gases and flue gases as hot as 1800°F. PCB residues (as DCB) ranging from ~ 1 ng to ~ 1 mg, corresponding to concentrations of < 1 ng/dscm and 306 μg/dscm, respectively, were determined. The mean percent deviation from the average for paired train samples was 13 ± 10% for all tests excluding runs 3 and 4 for the Blue River incinerator and runs 2A and 2B for the Dade Co. (NE) incinerator. PCB isomers were identified in all of the samples examined by GC/MS (approximately 50% of the total samples). The PCB verifications are described in Section 3.3.

3.3 Confirmation of PCB Residues from Incinerators

PCB residues were verified in all of the more than 50% of the incinerator samples examined. Extracts were concentrated to 1 ml by evaporation with a gentle stream of dry nitrogen prior to SIM-GC/MS examination. The chromatographic system utilized was that described in Section 2.1.1. Intensities of ions characteristic of PCB compounds were monitored. Coincident peaks in the ion chromatograms with relative intensities corresponding to those of the PCB compounds and at appropriate retention times were criteria for PCB verification. As examples of the verification, chromatograms for Aroclor 1254, Sample 2A from the Rollins, Inc., industrial incinerator, and Sample 2 from the Blue River sewage sludge incinerator are shown below.

Figures 12, 13, and 14 show SIM-GC/MS chromatograms for Aroclor 1254. Tetrachlorobiphenyls are shown in the plots of m/e 290 and 292 in Figure 12. Peaks eluting prior to ~ 2.5 min represent the tetrachlorobiphenyls. Peaks eluting after 2.5 min likely represent hexachlorobiphenyls since m/e 290 and 292 are prominent fragment ions in their mass spectra. Figure 13, chromatograms for m/e 324 and 326, shows the presence of pentachlorobiphenyls in Aroclor 1254 and Figure 14 shows hexachlorobiphenyls. Note the coincidence of the hexachlorobiphenyl peaks with the later eluting peaks in Figure 12.

The SIM-GC/MS chromatograms for Sample 2A from the Rollins, Inc., industrial incinerator are shown in Figures 15, 16, and 17. The peaks eluting at ~ 0.8 min on the m/e 290 and 292 plots (Figure 15) do not represent a tetrachlorobiphenyl since the ratio of ion intensities is not correct. However, peaks on the other plots (Figures 15, 16, and 17) indicate the presence of several tetra-, penta-, and hexachlorobiphenyls.

SIM-GC/MS chromatograms of the impinger extract from Sample 2 from the Blue River incinerator are shown in Figures 18, 19, and 20. Tetra- and pentachlorobiphenyls were identified along with a trace of hexachlorobiphenyl.

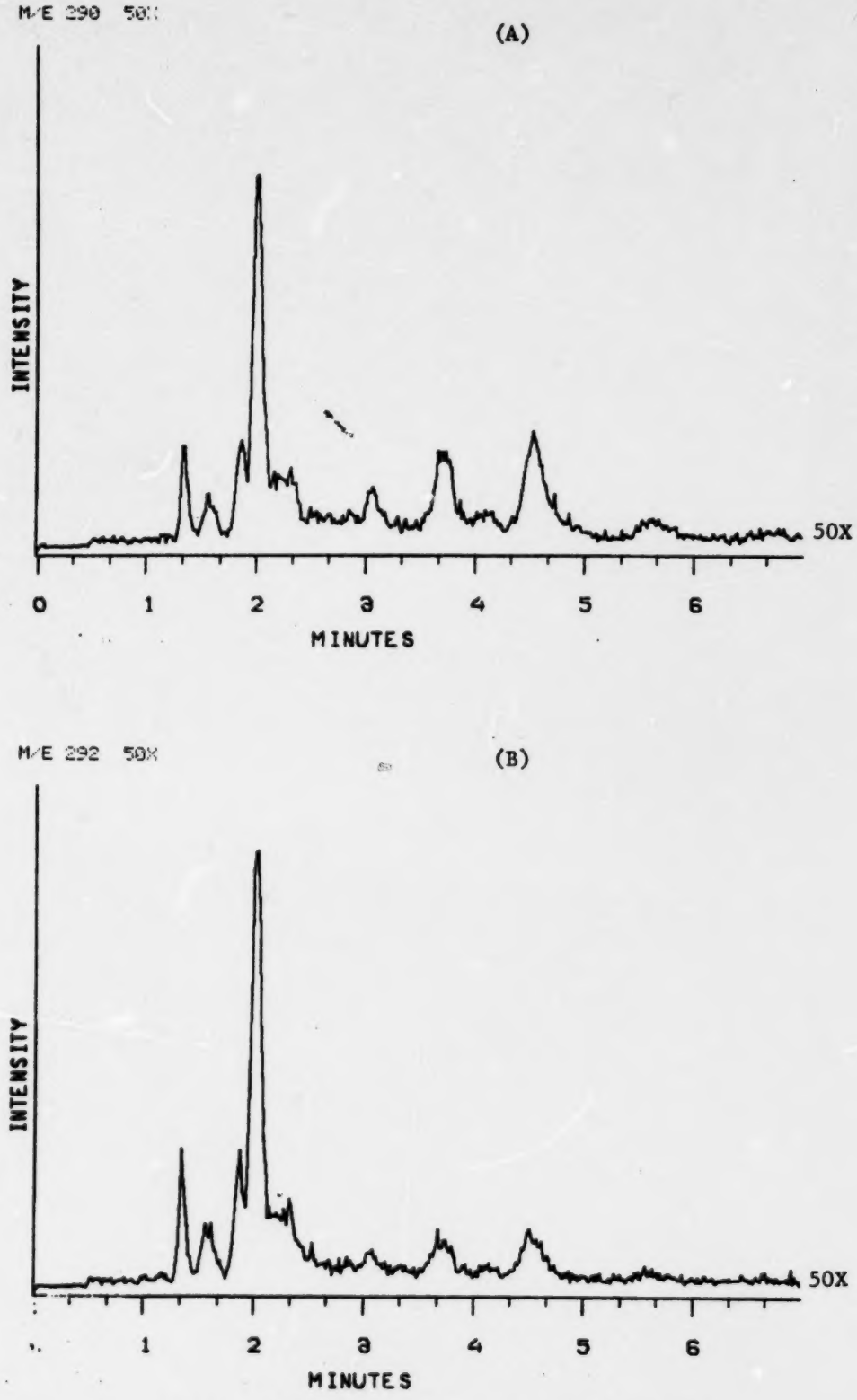

Figure 12 - SIM-GC/MS Chromatograms of m/e 290 (A) and 292 (B) for 2.0 ng Aroclor 1254

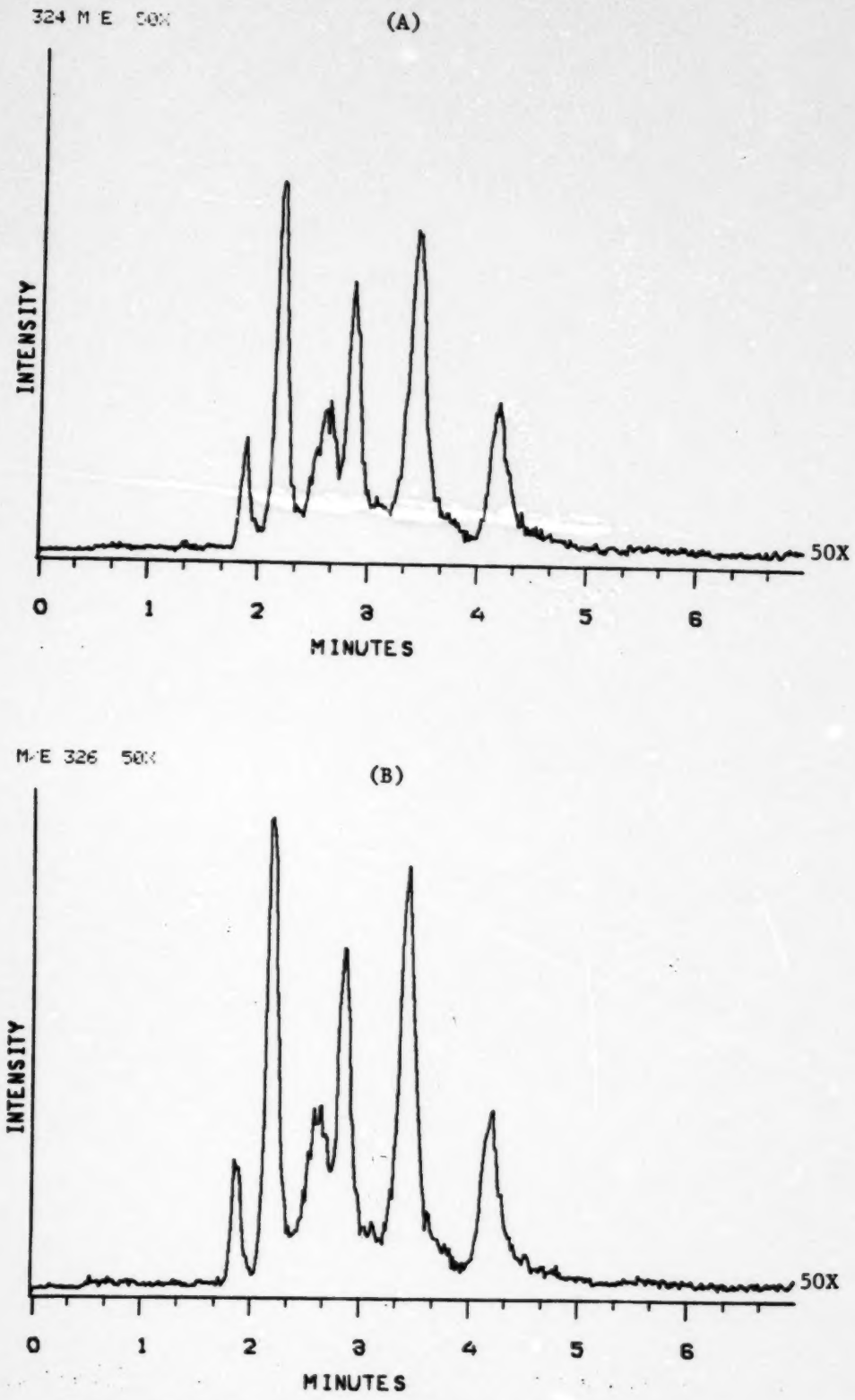

Figure 13 - SIM-GC/MS Chromatograms of m/e 324 (A) and 326 (B) for 2.0 ng Aroclor 1254

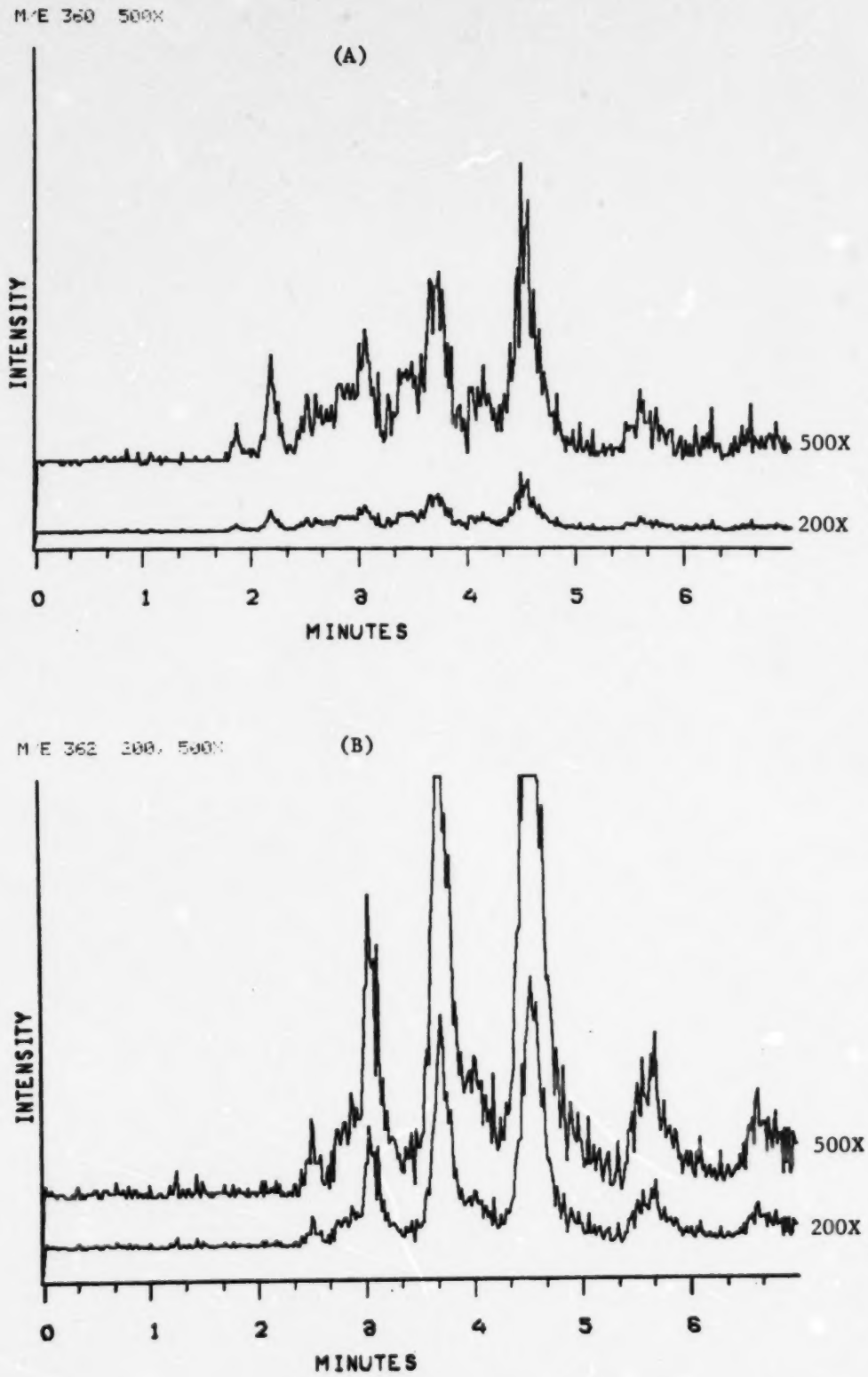

Figure 14 - SIM-GC/MS Chromatograms of m/e 360 (A) and 362 (B) for 2.0 ng Aroclor 1254

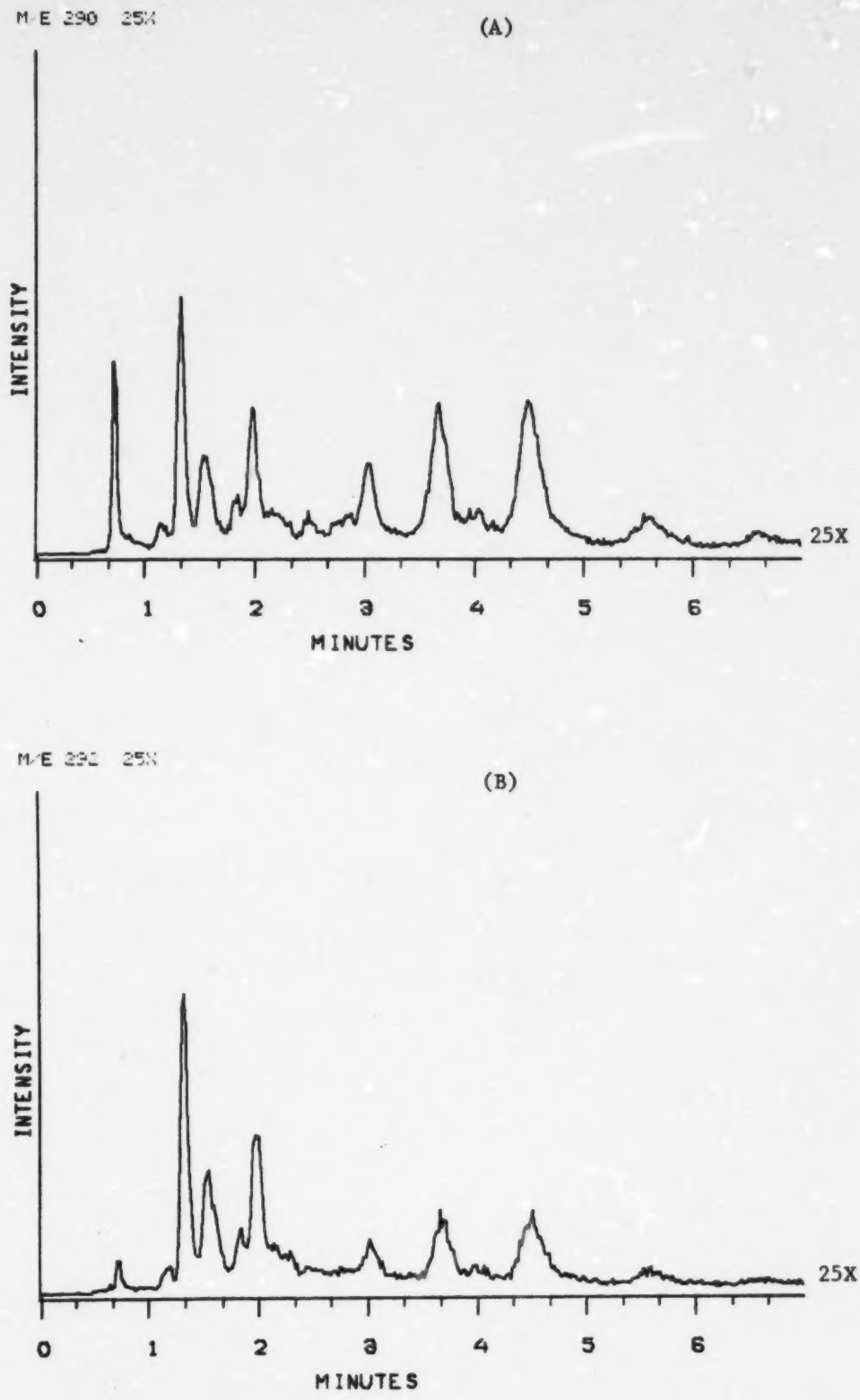

Figure 15 - SIM-GC/MS Chromatograms of m/e 290 (A) and 292 (B) for Sample 2A from the Rollins Industrial Incinerator

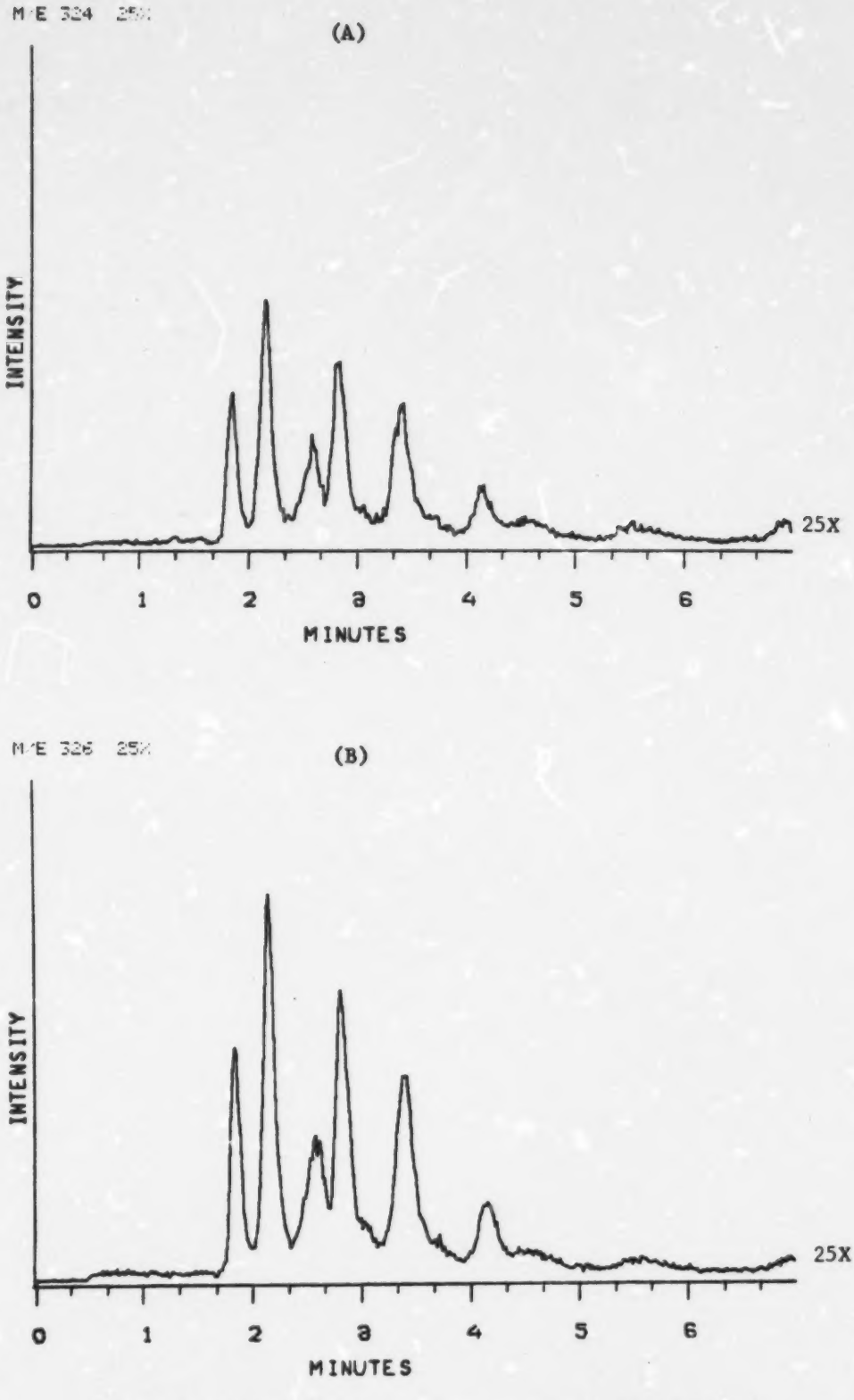

Figure 16 - SIM-GC/MS Chromatograms of m/e 324 (A) and 326 (B) for Sample 2A from the Rollins Industrial Incinerator

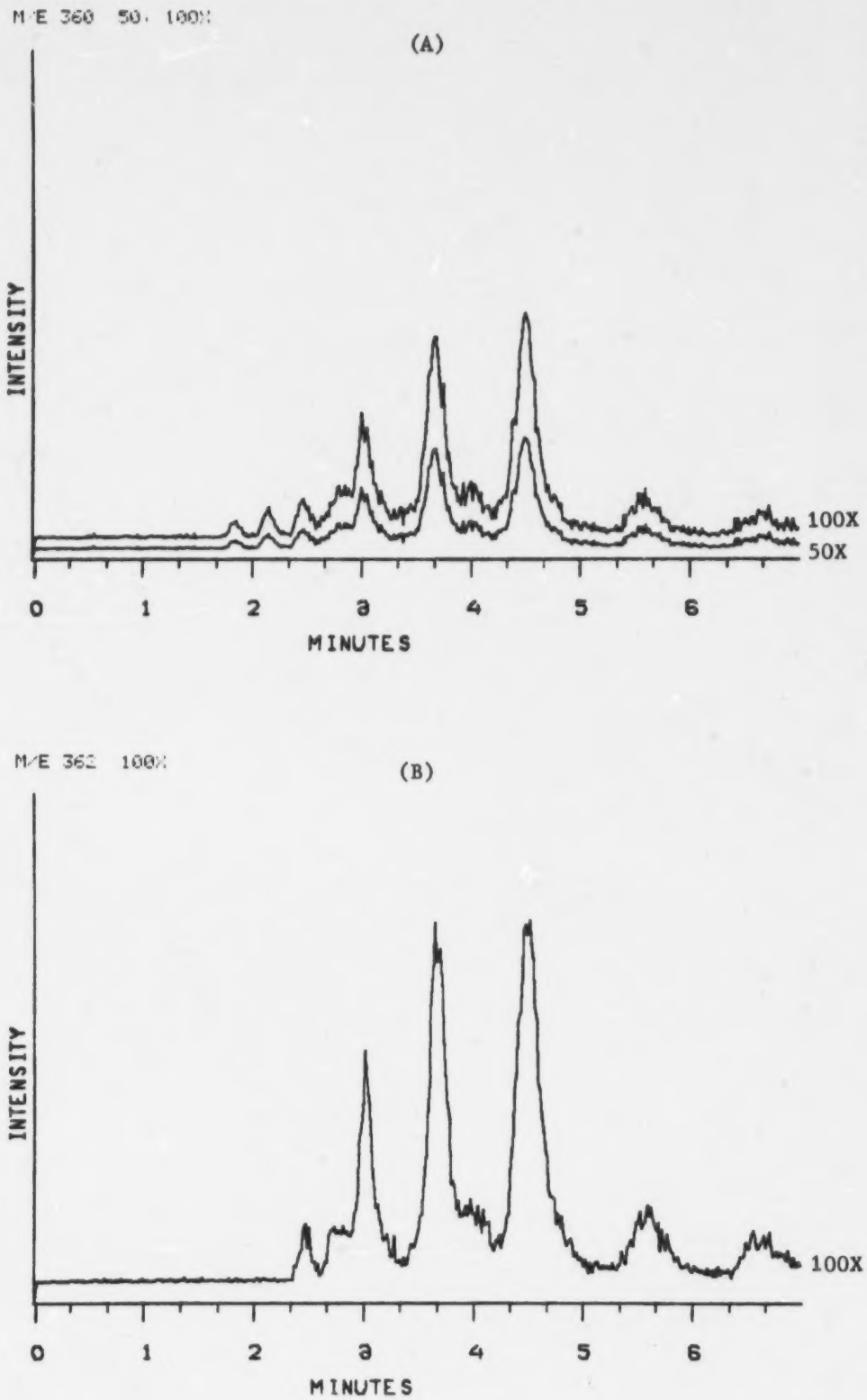

Figure 17 - SIM-GC/MS Chromatograms of m/e 360 (A) and 362 (B) for Sample 2A from the Rollins Industrial Incinerator

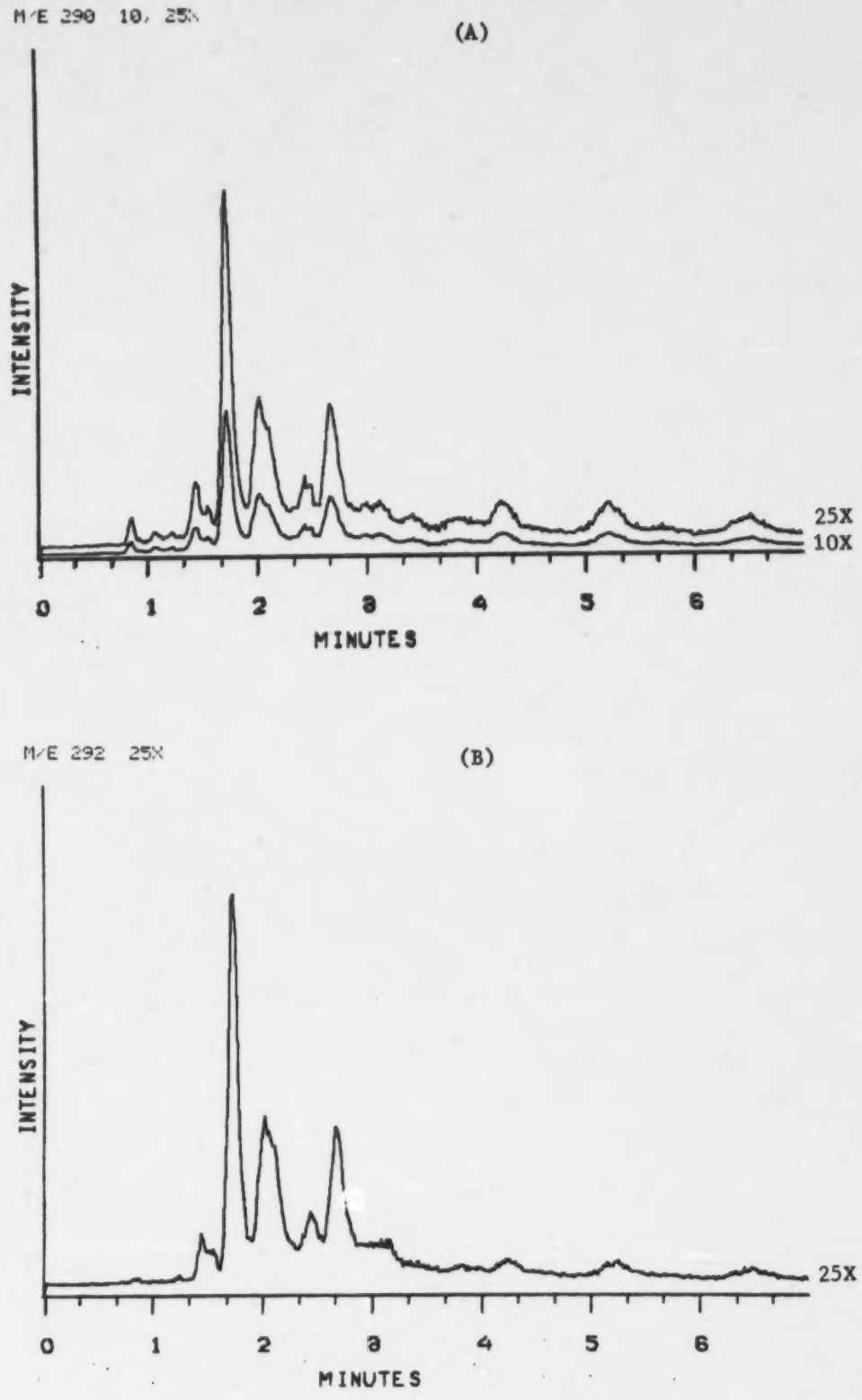

Figure 18 - SIM-GC/MS Chromatograms of m/e 290 (A) and 292 (B) for Sample 2 from the Blue River Sewage Sludge Incinerator

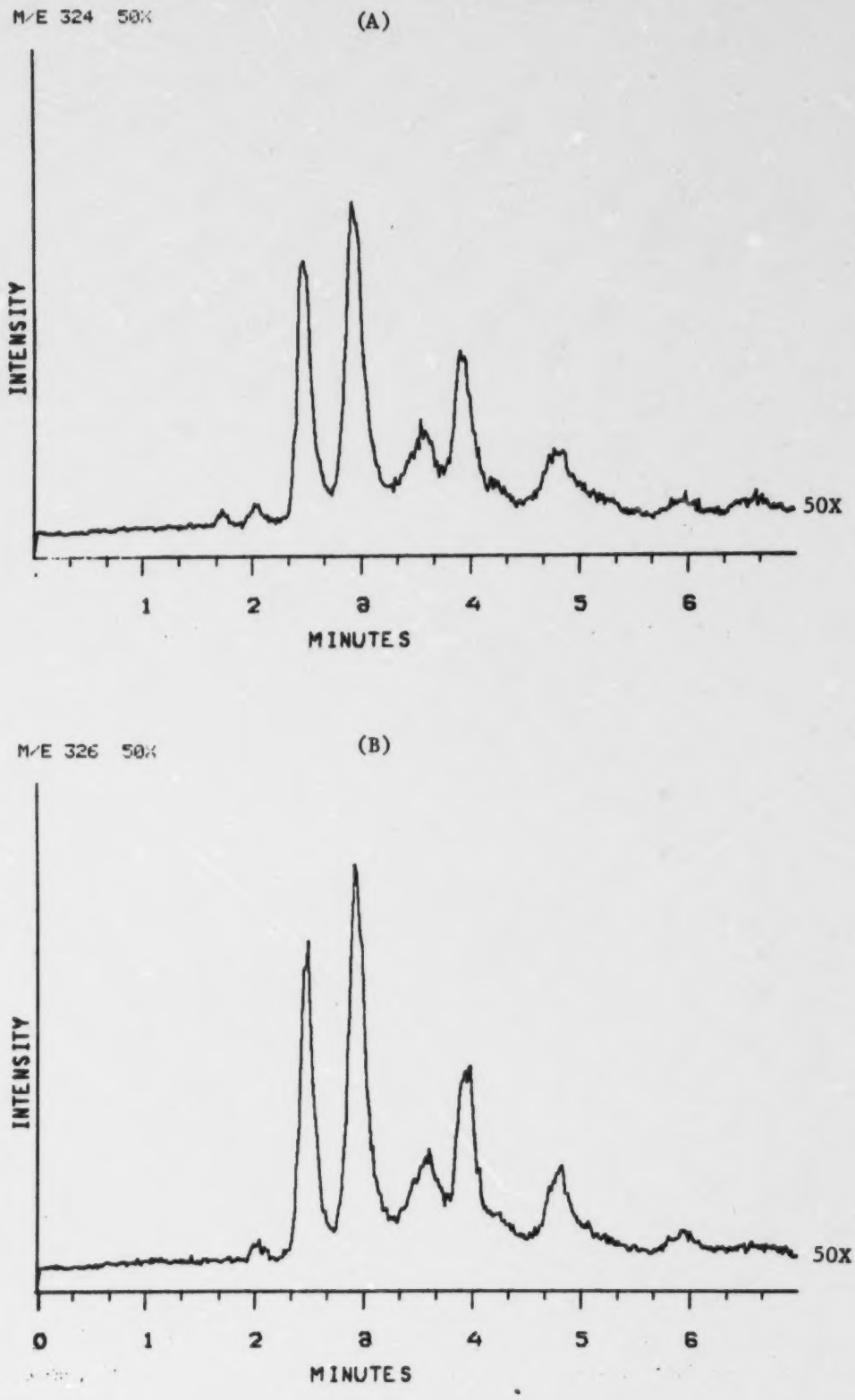

Figure 19 - SIM-GC/MS Chromatograms of m/e 324 (A) and 326 (B) for Sample 2 from the Blue River Sewage Sludge Incinerator

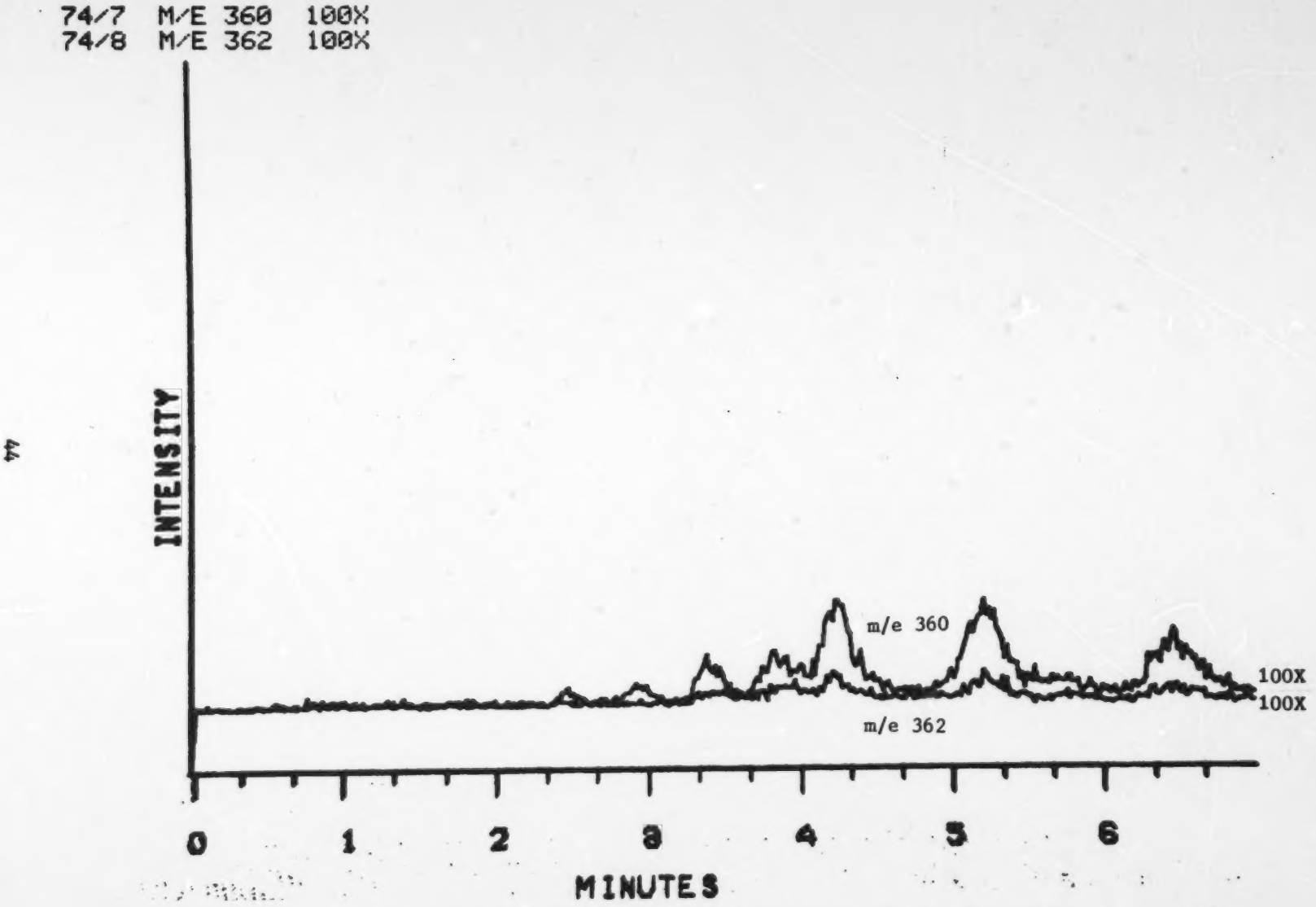

Figure 20 - SIM-GC/MS Chromatogram of m/e 360(A) and 362(B) for Sample 2 from the Blue River Sewage Sludge Incinerator

4.0 APPLICATION OF THE PCB METHOD TO EMISSIONS FROM CAPACITOR- AND TRANSFORMER-FILLING PLANTS

4.1 Method Adaptation

Gaseous emissions from capacitor- and transformer-filling plants are generally much easier to sample for PCB residues than emissions from incineration plants. Air is exhausted from filling rooms at temperatures and moisture contents near ambient and is less likely to contain excessive quantities of other organics. For these cases, the sampling train was simplified by removing the water-cooled probe and ice-cooled impingers. Hence, the sampling train was reduced to merely the adsorbent tube with associated pump and metering system and provisions for attaching a simple glass-lined probe to facilitate sampling of exhaust ducts. The simplicity of the sampling equipment allows elimination of sample recovery in the field. Sufficient adsorbent tubes and probes (where applicable) can be shipped to and from the sampling site to reduce chances of contamination during field sample recovery. Since the PCB residue collected may often closely resemble the particular commercial PCB mixture employed in the plant operations, the sampled residue may be quantitated against standard solutions of the appropriate commercial PCB mixture. In the event that the sampled residue does not closely resemble the mixture used in the plant, total PCBs may be assayed by the perchlorination procedures described for incinerator PCB residues. These modifications of the incinerator method are described in Part B of the appendix to this report.

4.2 Field Evaluations

The proposed PCB method for emissions from capacitor- and transformer-filling plants was evaluated by testing at two capacitor-filling plants herein designated A and B. For the purposes of these evaluations the ambient air in the filling rooms were sampled rather than exhausted air. The sampling systems were operated in tandem, positioned between the capacitor impregnation tanks, to provide duplicate samples. Sampling was conducted at 14 liters/min for 30 min to 4 hr to obtain a range of amounts of PCBs sampled. To check for PCB breakthrough, one of each of the duplicate trains utilized at Plant B was fitted with an additional Florisil tube connected in series to the primary adsorbent tube. For evaluation purposes, all samples from both plants were assayed by the perchlorination procedure.

The results of these field evaluation tests are shown in Table 14. The PCB residues recovered from the second Florisil tubes of Samples 1A, 2A, and 3A from Plant B contained 0.05, 0.15, and 0.1% of the total residue collected from those samples. Even when sampling milligram quantities of PCBs at 14 liters/min over 2 hr, breakthrough of the PCBs was negligible. The average percent deviation from the mean for the paired trains was 1.5% for Plant A when the large deviation of Samples 2A and 2B was ignored. The average percent

TABLE 14

SUMMARY OF PCB RESULTS (AS DCB) FOR TWO CAPACITOR-FILLING PLANTS

Plant:	A						B					
Run Number:	1A	1B	2A	2B	3A	3B	1A	1B	2A	2B	3A	3B
Date:	2/7/77	2/7/77	2/8/77	2/8/77	2/8/77	2/8/77	2/15/77	2/15/77	2/15/77	2/15/77	2/15/77	2/15/77
Time:	13:00-17:00	13:00-17:00	7:00-9:00	7:00-9:00	9:05-10:05	9:05-10:05	7:10-9:10	7:10-9:10	9:15-10:15	9:15-10:15	10:20-10:50	10:20-10:20
Sampling period (hr)	4.0	4.0	2.0	2.0	1.0	1.0	2.0	2.0	1.0	1.0	0.50	0.50
Volume of gas sampled (scm)[a/]	3.29	3.29	1.69	1.69	0.836	0.836	1.66	1.66	0.830	0.830	0.414	0.414
Total PCBs in sample (µg, as DCB)	2,750	2,940	467.2	96.0	332.8	332.9	4,610	3,840	1,090	2,180	1,020	2,130
PCB concentration in sample (µg/scm, as DCB)	835	892	276	56.9	398	399	2,770	2,310	1,310	2,630	2,460	5,150
Average PCB concentration in sample (µg/scm, as DCB)	864		166		399		2,540		1,970		3,810	

a/ scm = Standard cubic meter.

deviation was 26% for Plant B samples, likely reflecting the error introduced in several dilutions of the extracts to obtain concentrations appropriate for EC-CG assay. Both plants could have been adequately sampled for shorter periods with lower sampling rates if challenging the method had not been the primary objective.

The variation in the samples from Plant A likely reflect the actual production operations. Whereas Plant B was operated 24 hr daily, Plant A was operated by a single 8-hr shift each day. Samples 2A and 2B were taken at the beginning of the shift while capacitor impregnation operations were being initiated. Samples 3A and 3B were taken during mid-morning and 1A and 1B were taken during mid to late afternoon and included the period during which the impregnation equipment was cleaned in preparation for cessation of operations for the day.

5.0 CONCLUSONS

The adaptation of the Method 5 train by removing the heated filter and adding an adsorbent tube produced an efficient, simple, and compact sampling system for determining PCB emissions from industrial, sewage sludge, and municipal refuse incinerators. Of the three solids evaluated as a PCB adsorbent, 30/60 mesh Florisil was selected over Tenax-GC and XAD-2 based on trapping efficiency and the preparations required to obtain acceptable blanks. From laboratory studies, sampling efficiencies of 86 to 92% for Aroclors were determined for the sampling train using Florisil.

The sample recovery and PCB analysis protocol developed was based on procedures widely used for PCB residues in environmental samples. PCB samples collected were perchlorination to decachlorobiphenyl (DCB) and the DCB assayed. Molar yields of DCB from Aroclor mixtures were generally 80 to 85%.

The method was tested by sampling nine incineration plants. Since inlet and outlet samples were collected, a wide variety of flue gases were encountered, including gases as hot as 1800°F and gases saturated with moisture. PCB concentrations ranging from 1 ng/dscm to > 300 μg/dscm (as DCB) were determined. The mean percent deviation from average determinations for duplicate samples was 13 ± 10%. The presence of PCB isomers was verified by SIM-GC/MS in all of the more than 50% of the samples examined.

The PCB method was modified to allow determination of PCB emissions from capacitor- and transformer-filling plants. The sampling train was modified by removing the ice-cooled impingers. The modified method was tested by sampling ambient air in impregnation rooms of two capacitor-filling plants. PCB levels ranging from 166 to > 2,500 $\mu g/m^3$ (as DCB) were determined. Milligram quantities of PCBs were collected in some samples. PCB breakthroughs of < 0.15% were determined for the Florisil adsorbent tube by sampling with two tubes connected in series.

Overall, this study demonstrates the suitability of 30/60 mesh Florisil for collecting PCB residues from a variety of airstreams and suggests an applicability to PCB sampling of ambient air that should be investigated.

The PCB method developed is contained in an appendix to this report.

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APPENDIX

(DRAFT METHOD)

DETERMINATION OF TOTAL POLYCHLORINATED BIPHENYL (PCB) EMISSIONS FROM STATIONARY SOURCES

PART A. INDUSTRIAL, SEWAGE SLUDGE, AND MUNICIPAL REFUSE INCINERATORS

1. Principle and Applicability

1.1 Principle. Gaseous and particulate PCBs are withdrawn isokinetically from the source using a sampling train. The PCBs are collected in the Florisil adsorbent tube and in the impingers in front of the adsorbent. The total PCBs in the train are determined by perchlorination to decachlorobiphenyl (DCB) and gas chromatographic determination of the DCB.

1.2 Applicability. This method is applicable for the determination of PCB emissions (both vaporous and particulate) from industrial, sewage sludge, and municipal refuse incinerators.

2. Range and Sensitivity

The range of the analytical method may be expanded considerably through concentration and/or dilution. The total method sensitivity is also highly dependent on the volume of gases sampled. However, the sensitivity of the total method as described here is about 10 ng DCB for each analytical replicate.

3. Interferences

Excessive quantities of acid-resistant organics may cause significant interferences obscuring the analysis of DCB in the perchlorinated extracts. Biphenyl, although unlikely to be present in samples from combustion sources, can form DCB in the perchlorination processes.

Throughout all stages of sample handling and analysis, care should be taken to avoid contact of samples and extracts with synthetic organic materials other than TFE® (polytetrafluoroethylene). Adhesives must not be used to hold TFE® liners on lids, and lubricating and sealing greases must not be used on any sample exposed portions of the sampling train.

4. Precision and Accuracy

From sampling with identical and paired sampling trains, the precision of the method has been determined to be 10 to 15% of the PCB concentration measured. Recovery efficiencies on source samples spiked with PCB compounds ranged from 85 to 95%.

5. Apparatus

5.1 Sampling Train. See Figure A-1; a series of four impingers with a solid adsorbent trap between the third and fourth impingers. The train may be constructed by adaptation from a Method 5 train. Descriptions of the train components are contained in the following subsections.

5.1.1 Probe nozzle--Stainless steel (316) with sharp, tapered leading edge. The angle of taper shall be ≤ 30 degrees and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. The wall thickness of the nozzle shall be less than or equal to that of 20 gauge tubing, i.e., 0.165 cm (0.065 in.) and the distance from the tip of the nozzle to the first bend or point of disturbance shall be at least two times the outside nozzle diameter. The nozzle shall be constructed from seamless stainless steel tubing. Other configurations and construction material may be used with approval from the Administrator.

5.1.2 Probe liner--Borosilicate or quartz glass equipped with a connecting fitting that is capable of forming a leak-free, vacuum tight connection without sealing greases; such as Kontes Glass Company "O" ring spherical ground ball joints (model K-671300) or University Research Glassware SVL teflon screw fittings.

A stainless steel (316) or water-cooled probe may be used for sampling high temperature gases with approval from the Administrator. A probe heating system may be used to prevent moisture condensation in the probe.

5.1.3 Pitot tube--Type S, or equivalent, attached to probe to allow constant monitoring of the stack gas velocity. The face openings of the pitot tube and the probe nozzle shall be adjacent and parallel to each other but not necessarily on the same plane, during sampling. The free space between the nozzle and pitot tube shall be at least 1.9 cm (0.75 in.). The free space shall be set based on a 1.3 cm (0.5 in.) ID nozzle, which is the largest size nozzle used.

The pitot tube must also meet the criteria specified in Method 2 and be calibrated according to the procedure in the calibration section of that method.

5.1.4 Differential pressure gauge--Inclined manometer capable of measuring velocity head to within 10% of the minimum measured value. Below a differential pressure of 1.3 mm (0.05 in.) water gauge, micromanometers with sensitivities of 0.013 mm (0.0005 in.) should be used. However,

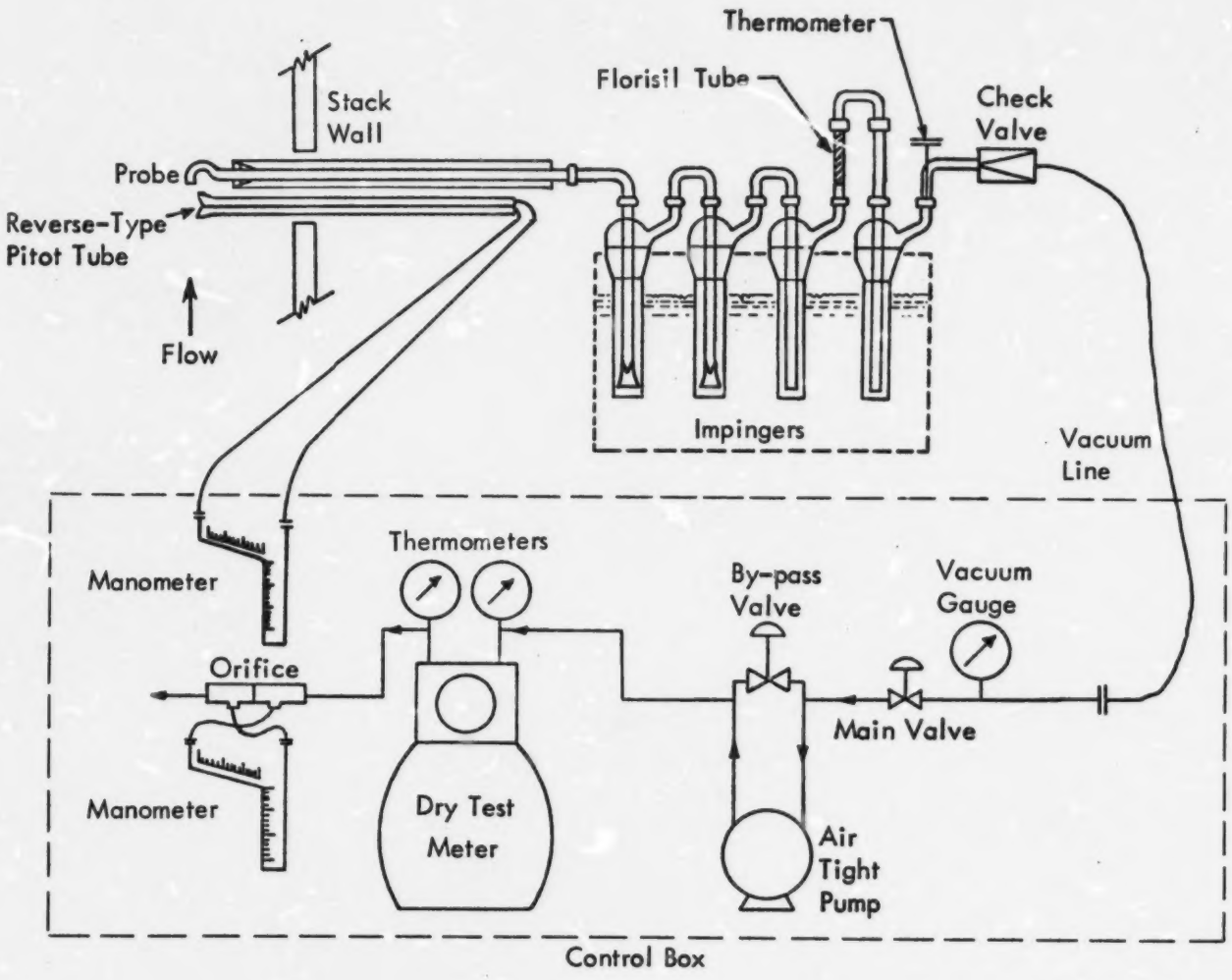

Figure A-1. PCB Sampling Train for Incinerators

micromanometers are not easily adaptable to field conditions and are not easy to use with pulsating flow. Thus, other methods or devices acceptable to the Administrator may be used when conditions warrant.

5.1.5 Impingers--Four impingers with connecting fittings able to form leak-free, vacuum tight seals without sealant greases when connected together as shown in Figure A-1. The first and second impingers are of the Greenburg-Smith design. The final two impingers are of the Greenburg-Smith design modified by replacing the tip with a 1.3 cm (1/2 in.) ID glass tube extending to 1.3 cm (1/2 in.) from the bottom of the flask.

5.1.6 Solid adsorbent tube--Glass with connecting fittings able to form leak-free, vacuum tight seals without sealant greases (Figure A-2). Exclusive of connectors, the tube has a 2.2 cm inner diameter, is at least 10 cm long, and has four deep indentations on the inlet end to aid in retaining the adsorbent. Ground glass caps (or equivalent) must be provided to seal the adsorbent-filled tube both prior to and following sampling.

5.1.7 Metering system--Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3°C (~ 5°F), dry gas meter with 2% accuracy at the required sampling rate, and related equipment, or equivalent, as required to maintain an isokinetic sampling rate and to determine sample volume. When the metering system is used in conjunction with a pitot tube, the system shall enable checks of isokinetic rates.

5.1.8 Barometer--Mercury, aneroid, or other barometers capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby weather bureau station, in which case the station value shall be requested and an adjustment for elevation differences shall be applied at a rate of -2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase.

5.2 Sample Recovery

5.2.1 Ground glass caps--To cap off adsorbent tube and the other sample exposed portions of the train.

5.2.2 Teflon FEP® wash bottle--Two, 500 ml, Nalgene No. 0023A59 or equivalent.

5.2.3 Sample storage containers--Glass bottles, 1 liter, with TFE®-lined screw caps.

5.2.4 Balance--Triple beam, Ohaus Model 7505 or equivalent.

5.2.5 Aluminum foil--Heavy duty.

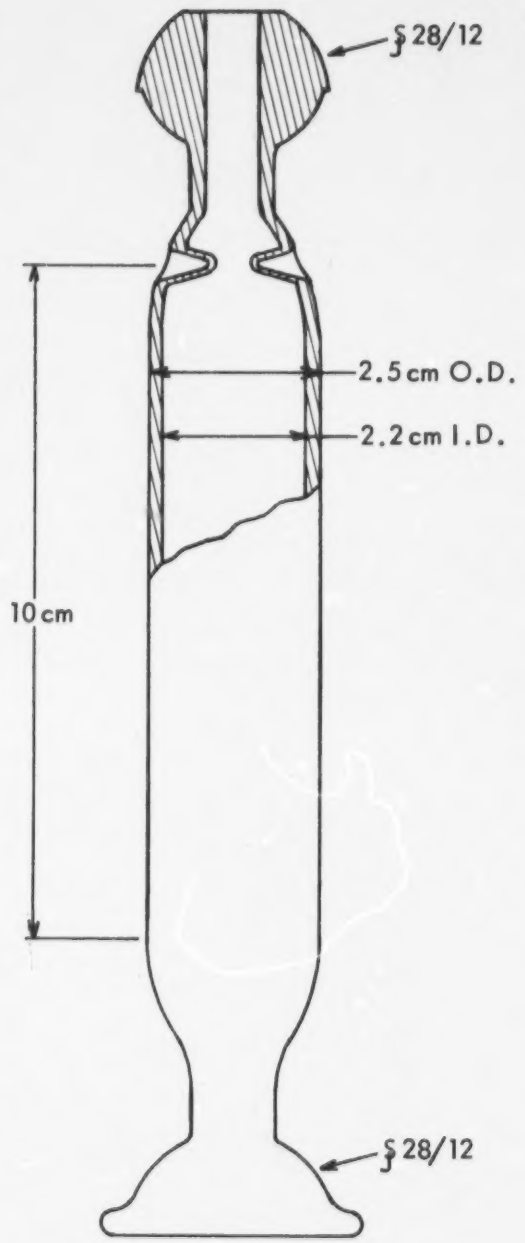

Figure A-2. Florisil Adsorbent Tube

5.2.6 Metal can--To recover used silica gel.

5.3 Analysis

5.3.1 Glass Soxhlet extractors--40 mm ID complete with 45/50 ℨ condenser, 24/40 ℨ 250 ml round bottom flask, heating mantle for 250 ml flask, and power transformer.

5.3.2 Teflon FEP wash bottle--Two, 500 ml, Nalgene No. 0023A59 or equivalent.

5.3.3 Separatory funnel--1,000 ml with TFE® stopcock.

5.3.4 Kuderna-Danish concentrators--500 ml.

5.3.5 Steam bath.

5.3.6 Separatory funnel--50 ml with TFE® stopcock.

5.3.7 Volumetric flask--25.0 ml, glass.

5.3.8 Volumetric flask--5.0 ml, glass.

5.3.9 Culture tubes--13 x 100 mm, glass with TFE®-lined screw caps.

5.3.10 Pipette--5.0 ml glass.

5.3.11 Aluminum block--Drilled to support culture tubes while heating.

5.3.12 Hot plate--Capable of heating to 200°C.

5.3.13 Teflon®-glass syringe--1 ml, Hamilton 1001 TLL or equivalent with Teflon® needle.

5.3.14 Syringe--10 µl, Hamilton 701N or equivalent.

5.3.15 Gas chromatograph--Fitted with electron capture detector capable of operation at 300°C and with 2 mm ID x 1.8 mm glass column packed with 3% OV-210 on 100/120 mesh inert support (e.g., Supelcoport®).

5.3.16 Electric muffle furnace--Capable of heating to 650°C.

5.3.17 Electric oven--Capable of heating to 150°C.

5.3.18 Disposable glass pipettes with bulbs--To aid transfer of the extracts.

5.3.19 Porcelain casserole--Capable of withstanding temperatures as high as 650°C.

6. Reagents

6.1 Sampling

6.1.1 Florisil--Floridin Co., 30/60 mesh, Grade A. The Florisil is cleaned by 8 hr Soxhlet extraction with hexane and then by drying for 8 hr in an oven at 110°C and is activated by heating to 650°C for 2 hr (not to exceed 3 hr) in a muffle furnace. After allowing to cool to near 110°C transfer the clean, active Florisil to a clean, hexane-washed glass jar and seal with a TFE®-lined lid. The Florisil should be stored at 110°C until taken to the field for use. Florisil that has been stored more than 1 month must be reactivated before use.

6.1.2 Glass wool--Cleaned by thorough rinsing with hexane, dried in a 110°C oven, and stored in a hexane-washed glass jar with TFE®-lined screw cap.

6.1.3 Water--Deionized, then glass-distilled, and stored in hexane-rinsed glass containers with TFE®-lined screw caps.

6.1.4 Silica gel--Indicating type, 6-16 mesh. If previously used, dry at 175°C for 2 hr. New silica gel may be used as received.

6.1.5 Crushed ice.

6.2 Sample Recovery

6.2.1 Acetone--Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.2.2 Hexane--Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.3 Analysis

6.3.1 Hexane--Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.3.2 Acetone--Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.3.3 Water--Deionized and then glass-distilled, stored in hexane-rinsed glass containers with TFE®-lined screw caps.

6.3.4 Sodium sulfate (Na_2SO_4)--Anhydrous, granular. Clean by overnight Soxhlet extraction with hexane, drying in a 110°C oven, and then heating to 650°C for 2 hr. Store in 110°C oven or in glass jar closed with TFE®-lined screw cap.

6.3.5 Sulfuric acid (H_2SO_4)--Concentrated, ACS reagent grade or equivalent.

6.3.6 Antimony pentachloride ($SbCl_5$)--Baker Analyzed Reagent or equivalent.

6.3.7 Hydrochloric acid (HCl) solution--ACS reagent grade or equivalent, 50% in water.

6.3.8 Glass wool--Cleaned by thorough rinsing with hexane, dried in a 110°C oven, and stored in a hexane-rinsed glass jar with TFE®-lined cap.

6.3.9 Decachlorobiphenyl--RFP Corp., No. RPC-60, or equivalent.

6.3.10 Compressed nitrogen--Prepurified.

6.3.11 Carborundum boiling stones--Hengar Co. No. 133-B or equivalent, rinsed with hexane.

7. Procedure

Caution: Section 7.1.1 should be done in the laboratory.

7.1 Sampling. The sampling shall be conducted by competent personnel experienced with this test procedure and cognizant of the constraints of the analytical techniques for PCBs, particularily contamination problems.

7.1.1 Pretest preparation. All train components shall be maintained and calibrated according to the procedure described in APTD-0576, unless otherwise specified herein.

7.1.1.1 Cleaning glassware. All glass parts of the train upstream of and including the adsorbent tube, should be cleaned as described in Section 3A of the 1974 issue of "Manual of Analytical Methods for Analysis of Pesticide Residues in Human and Environmental Samples." Special care should be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. These grease residues should be removed by soaking several hours in a chromic acid cleaning solution prior to routine cleaning as described above.

7.1.1.2 Solid adsorbent tube. Weigh 7.5 g of Florisil, activated within the last 30 days and still warm from storage in a 110°C oven, into the adsorbent tube (pre-rinsed with hexane) with a glass wool plug in the downstream end. Place a second glass wool plug in the tube to hold the sorbent in the tube. Cap both ends of the tube with ground glass caps. These caps should not be removed until the tube is fitted to the train immediately prior to sampling.

7.1.2 Preliminary determinations. Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2 and moisture content using Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate calculations. Estimates may be used. However, final results will be based on actual measurements made during the test.

Determine the molecular weight of the stack gases using Method 3.

Select a nozzle size based on the maximum velocity head so that isokinetic sampling can be maintained at a rate less than 0.75 cfm. It is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size.

Select a suitable probe length such that all traverse points can be sampled. Consider sampling from opposite sides for large stacks to reduce the length of probes.

Select a sampling time appropriate for total method sensitivity and the PCB concentration anticipated. Sampling times should generally fall within a range of 2 to 4 hr.

It is recommended that a buzzer-timer be incorporated in the control box (see Figure 1) to alarm the operator to move the probe to the next sampling point.

In some circumstances, e.g., short batch processes, it may be necessary to sample through two or more batches to obtain sufficient sample volume. In these cases, sampling should cease during loading/unloading of the furnace.

7.1.3 Preparation of collection train. During preparation and assembly of the sampling train, keep all train openings where contamination can enter covered until just prior to assembly or until sampling is about to begin. Immediately prior to assembly, rinse all parts of the train upstream of the adsorbent tube with hexane.

Mark the probe with heat resistant tape or by some other method at points indicating the proper distance into the stack or duct for each sampling point.

Place 200 ml of water in each of the first two impingers, and leave the third impinger empty. CAUTION: do not use sealant greases in assembling the train. If the preliminary moisture determination shows that the stack gases are saturated or supersaturated, one or two additional empty impingers should be added to the train between the third impinger and the Florisil tube. See Section 10.1. Place approximately 200 to 300 g or more, if necessary, of silica gel in the last impinger. Weigh each impinger (stem included) and record the weights on the impingers and on the data sheet.

Unless otherwise specified by the Administrator, attach a temperature probe to the metal sheath of the sampling probe so that the sensor is at least 2.5 cm behind the nozzle and pitot tube and does not touch any metal.

Assemble the train as shown in Figure A-1. Through all parts of this method use of sealant greases such as stopcock grease to seal ground glass joints must be avoided.

Place crushed ice around the impingers.

7.1.4 Leak check procedure--After the sampling train has been assembled, turn on and set (if applicable) the probe heating system(s) to reach a temperature sufficient to avoid condensation in the probe. Allow time for the temperature to stabilize. Leak check the train at the sampling site by plugging the nozzle and pulling a 380 mm Hg (15 in. Hg) vacuum. A leakage rate in excess of 4% of the average sampling rate of 0.0057 m^3/min (0.02 cfm) whichever is less, is unacceptable.

The following leak check instruction for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with bypass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the bypass valve until 380 mm Hg (15 in. Hg) vacuum is reached. Do not reverse direction of bypass valve. This will cause water to back up into the probe. If 380 mm Hg (15 in. Hg) is exceeded, either leak check at this higher vacuum or end the leak check as described below and start over.

When the leak check is completed, first slowly remove the plug from the inlet to the probe and immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the probe.

Leak checks shall be conducted as described above prior to each test run and at the completion of each test run. If leaks are found to be in excess of the acceptable rate, the test will be considered invalid. To reduce lost time due to leakage occurrences, it is recommended that leak checks be conducted between port changes.

7.1.5 Train operation--During the sampling run, an isokinetic sampling rate within 10%, or as specified by the Administrator, of true isokinetic shall be maintained. During the run, do not change the nozzle or any other part of the train in front of and including the Florisil tube.

For each run, record the data required on the data sheets. An example is shown in Figure A-3. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, and when sampling is halted. Take other data point readings at least once at each sample point during each time increment and additional readings when significant changes (20% variation in velocity head readings) necessitate additional adjustments in flow rate. Be sure to level and zero the manometer.

Clean the portholes prior to the test run to minimize chance of sampling deposited material. To begin sampling, remove the nozzle cap, verify (if applicable) that the probe heater is working and up to temperature, and that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs are available for sampling trains using type S pitot tubes with 0.85 ± 0.02 coefficients (C_p), and when sampling in air or a stack gas with equivalent density (molecular weight, M_d, equal to 29 ± 4), which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. APTD-0576 details the procedure for using these nomographs. If C_p and M_d are outside the above stated ranges, do not use the nomograph unless appropriate steps are taken to compensate for the deviations.

When the stack is under significant negative pressure (height of impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack to avoid water backing into the probe. If necessary, the pump may be turned on with the coarse adjust valve closed.

When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

Traverse the stack cross section, as required by Method 1 or as specified by the Administrator. To minimize chance of extracting deposited material, be careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the portholes.

FIELD DATA

PLANT _____
DATE _____
SAMPLING LOCATION _____
SAMPLE TYPE _____
RUN NUMBER _____
OPERATOR _____
AMBIENT TEMPERATURE _____
BAROMETRIC PRESSURE _____
STATIC PRESSURE, (P_s) _____
FILTER NUMBER (s) _____

PROBE LENGTH AND TYPE _____
NOZZLE I.D. _____
ASSUMED MOISTURE, % _____
SAMPLE BOX NUMBER _____
METER BOX NUMBER _____
METER $\Delta H_@$ _____
C FACTOR _____
PROBE HEATER SETTING _____
HEATER BOX SETTING _____
REFERENCE Δp _____

SCHEMATIC OF TRAVERSE POINT LAYOUT

READ AND RECORD ALL DATA EVERY _____ MINUTES

TRAVERSE POINT NUMBER	SAMPLING TIME, min / CLOCK TIME (24-hr CLOCK)	GAS METER READING (V_m), ft^3	VELOCITY HEAD (Δp_s), in. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O		STACK TEMPERATURE (T_s), °F	DRY GAS METER TEMPERATURE		PUMP VACUUM, in. Hg	SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
				DESIRED	ACTUAL		INLET ($T_{m\ in}$), °F	OUTLET ($T_{m\ out}$), °F			

COMMENTS:

Figure A-3. Field Data Sheet

EPA (Dur) 235
4 72

During the test run, make periodic adjustments to keep the probe temperature at the proper value. Add more ice and, if necessary, salt to the ice bath, to maintain a temperature of less than 20°C (68°F) at the impinger/silica gel outlet, to avoid excessive moisture losses. Also, periodically check the level and zero of the manometer.

If the pressure drop across the train becomes high enough to make isokinetic sampling difficult to maintain, the test run should be terminated. Under no circumstances should the train be disassembled during a test run to determine and correct causes of excessive pressure drops.

At the end of the sample run, turn off the pump, remove the probe and nozzle from the stack, and record the final dry gas meter reading. Perform a leak check.* Calculate percent isokinetic (see calculation section) to determine whether another test run should be made. If there is difficulty in maintaining isokinetic rates due to source conditions, consult with the Administrator for possible variance on the isokinetic rates.

7.1.6 Blank train--For each series of test runs, set up a blank train in a manner identical to that described above, but with the nozzle capped with aluminum foil and the exit end of the last impinger capped with a ground glass cap. Allow the train to remain assembled for a period equivalent to one test run. Recover the blank sample as described in Section 7.2.

7.2 Sample recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle. Remove the probe from the train and close off both ends with aluminum foil. Cap off the inlet to the train with a ground glass cap.

Transfer the probe and impinger assembly to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

Inspect the train prior to and during disassembly and note any abnormal conditions. Treat the samples as follows:

7.2.1 Adsorbent tube--Remove the Florisil tube from the train and cap it off with ground glass caps.

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* With acceptability of the test run to be based on the same criterion as in 7.1.4.

7.2.2 Sample container No. 1--Remove the first three impingers. Wipe off the outside of each impinger to remove excessive water and other debris, weigh (stem included), and record the weight on data sheet. Pour the contents directly into container No. 1 and seal.

7.2.3 Sample container No. 2--Rinse each of the first three impingers sequentially first with 30 ml acetone and then with 30 ml hexane, and put the rinses into container No. 2. Quantitatively recover material deposited in the probe using 100 ml acetone and then 100 ml hexane and add these rinses to container No. 2 and seal.

7.2.4 Silica gel container--Remove the last impinger, wipe the outside to remove excessive water and other debris, weigh (stem included), and record weight on data sheet. Transfer the contents to the used silica gel can.

7.3 Analysis. The analysis of the PCB samples should be conducted by chemical personnel experienced in determinations of trace organics utilizing sophisticated, instrumental techniques. All extract transfers should be made quantitatively by rinsing the apparatus at least three times with hexane and adding the rinses to the receiving container. A boiling stone should be used in all evaporative steps to control "bumping."

7.3.1 Extraction

7.3.1.1 Adsorbent tube. Expel the entire contents of the adsorbent tube directly onto a glass wool plug in the sample holder of a Soxhlet extractor. Although no extraction thimble is required, a glass thimble with a coarse-fritted bottom may be used.

Rinse the tube with 5 ml acetone and then with 15 ml hexane and put these rinses into the extractor. Assemble the extraction apparatus and extract the adsorbent with 170 ml hexane for at least 4 hr. The extractor should cycle 10 to 14 times per hour. After allowing the extraction apparatus to cool to ambient temperature, transfer the extract into a Kuderna-Danish evaporator.

Evaporate the extract to about 5 ml on a steam bath and allow the evaporator to cool to ambient temperature before disassembly. Transfer the extract to a 50-ml separatory funnel and set the funnel aside.

7.3.1.2 Sample container No. 1. Transfer the aqueous sample to a 1,000-ml separatory funnel. Rinse the container with 20 ml acetone and then with two 20-ml portions of hexane, adding the rinses to the separatory funnel.

Extract the sample with three 100 ml portions of hexane, transferring the sequential extracts to a Kuderna-Danish evaporator.

Evaporate the extract to about 5 ml and allow the evaporator to cool to ambient temperature before disassembly. Filter the extract through a micro column of anhydrous sodium sulfate into the 50 ml separatory funnel containing the corresponding Florisil extract. The micro column is prepared by placing a small plug of glass wool in the bottom of the large portion of a disposable pipette and then adding anhydrous sodium sulfate until the tube is about half full.

7.3.1.3 Sample container No. 2. Transfer the organic solution into a 1,000 ml separatory funnel. Rinse the container with two 20 ml portions of hexane and add the rinses to the separatory funnel. Wash the sample with three 100 ml portions of water. Discard the aqueous layer and transfer the organic layer to a Kuderna-Danish evaporator.

Evaporate the extract to about 5 ml and allow the evaporator to cool to ambient temperature before disassembly. Filter the extract through a micro column of anhydrous sodium sulfate into the 50 ml separatory funnel containing the corresponding Florisil and impinger extracts.

7.3.2 Extract cleanup--Clean the combined extracts (in 50 ml separatory funnel) by shaking with 5 ml concentrated sulfuric acid. Allow the acid layer to separate and drain it off.

Transfer the hexane layer to a Kuderna-Danish evaporator and evaporate to about 5 ml. Allow the evaporator to cool to ambient temperature before disassembly.

The extract should be essentially colorless. If it still shows significant color, additional cleanup may be required before assaying for PCBs. In this event, further clean the extract by liquid chromatography on Florisil according to procedures described in Section 5A of the 1974 issue of "Manual of Analytical Methods for Analysis of Pesticide Residues in Human and Environmental Samples" Reduce the Florisil eluant to about 10 ml by Kuderna-Danish evaporation techniques described above.

Transfer the cleaned extract to a 25 ml volumetric flask and dilute to volume with hexane. Pipette three 5.0 ml aliquots into culture tubes for perchlorination. Retain the remaining 10 ml for later verification, if required (see Section 10.2).

7.3.3 Extract perchlorination--Evaporate the aliquots in the culture tubes just to dryness with a gentle stream of dry nitrogen. If the aliquots will not evaporate to dryness, refer to Section 10.3 concerning special cases. Add 0.2 ml antimony pentachloride with a 1 ml glass-TFE® syringe and

seal the tube with a TFE®-lined screw cap. Heat the reaction mixture to 160°C for 2 hr by placing the tube in a hole in an aluminum block on a hot plate.

Allow the tube to cool to ambient room temperature before adding about 2 ml of 50% HCl in water to destroy residual antimony pentachloride. This is a convenient "stopping point" in the perchlorination procedure.

Extract the reaction mixture by adding about 1 ml hexane to the tube, shake, and allow layers to separate. Remove the upper hexane layer with a disposable pipette and filter through a micro column of anhydrous sodium sulfate directly into a 5 ml volumetric flask. Repeat the extraction three times for a total of four extractions. Dilute the extract to volume with hexane.

7.3.4 PCB determination--Assay the perchlorinated extracts for decachlorobiphenyl (DCB) by gas chromatographic comparison with DCB standard solutions and correct this result for the DCB concentration determined for the blank train. (Column temperature and carrier gas flow parameters of 240°C and 30 ml/min, are typically appropriate. The concentrations of the standard solutions should allow fairly close comparison with DCB in the sample extracts. Standards near 25 to 50 picograms/microliter may be appropriate.)

8. Calibration

Maintain a laboratory log of all calibrations.

8.1 Sampling Train

8.1.1 Probe nozzle--Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make three separate measurements using different diameters each time and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.).

When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use.

Each nozzle shall be permanently and uniquely identified.

8.1.2 Pitot tube--The pitot tube shall be calibrated according to the procedure outlined in Method 2.

8.1.3 Dry gas meter and orifice meter--Both meters shall be calibrated according to the procedure outlined in APTD-0576. When diaphragm

pumps with bypass valves are used, check for proper metering system design by calibrating the dry gas meter at an additional flow rate of 0.0057 m^3/min (0.2 cfm) with the bypass valve fully opened and then with it fully closed. If there is more than $\pm$ 2% difference in flow rates when compared to the fully closed position of the bypass valve, the system is not designed properly and must be corrected.

8.1.4 Probe heater calibration--The probe heating system shall be calibrated according to the procedure contained in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used.

8.1.5 Temperature gauges--Calibrate dial and liquid filled bulb thermometers against mercury-in-glass thermometers. Thermocouples should be calibrated in constant temperature baths.

8.2 Analytical Apparatus

8.2.1 Gas chromatograph--Prepare a working curve from at least five standard injections of different volumes of the DCB standard.

9. Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

9.1 Nomenclature

G_n = Corrected weight of DCB in nth perchlorinated aliquot (n = 1, 2, 3), µg.

G_s = Total weight of PCBs (as DCB) in sample, µg.

C_s = Concentration of PCBs in stack gas, µg/m^3, corrected to standard conditions of 20°C, 760 mm Hg (68°F, 29.92 in. Hg) on dry basis.

A_n = Cross-sectional area of nozzle, m^2 (ft^2).

B_{ws} = Water vapor in the gas stream, proportion by volume.

I = Percent of isokinetic sampling.

M_w = Molecular weight of water, 18 g/g-mole (18 lb/lb-mole).

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in Hg).

R = Ideal gas constant, 0.06236 mm Hg-m^3/°K-g-mole (21.83 in. Hg-ft^3/°R-lb-mole).

T_m = Absolute average dry gas meter temperature °K (°R).

T_s = Absolute average stack gas temperature °K (°R).

T_{std} = Standard absolute temperature, 293°K (528°R).

V_{lc} = Total volume of liquid collected in impingers and silica gel, ml. volume of water collected equals the weight increase in grams times 1 ml/gram

V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter corrected to standard conditions, dscm (dscf).

$V_{w(std)}$ = Volume of water vapor in the gas sample corrected to standard conditions, scm (scf).

V_t = Total volume of sample, ml.

V_s = Stack gas velocity, calculated by EPA Method 2, m/sec (ft/sec).

ΔH = Average pressure differential across the orifice meter, mm H_2O (in. H_2O).

ρ_w = Density of water, 1 g/ml (0.00220 lb/ml).

θ = Total Sampling time, min.

13.6 = Specific gravity of mercury.

60 = Sec/min.

100 = Conversion to percent.

9.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure A-3).

9.3 Dry gas volume. Correct the sample volume measured by the dry gas meter to standard conditions [20°C, 760 mm Hg (68°F, 29.92 in. Hg)] by using Equation A-1).

$$V_{m(std)} = V_m \frac{T_{std}}{T_m} \left[\frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}} \right] = K V_m \frac{P_{bar} + \frac{\Delta H}{13.6}}{T_m}$$

Equation A-1

where $K = 0.3855$ °K/mm Hg for metric units

$= 17.65$ °R/in. Hg for English units

9.4 Volume of water vapor

$$V_{w(std)} = V_{lc} \frac{\rho_w}{M_w} \frac{RT_{std}}{P_{std}} = K V_{lc}$$

Equation A-2

where $K = 0.00134$ m^3/ml for metric units

$= 0.0472$ ft^3/ml for English units

9.5 Moisture content

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}}$$

Equation A-3

If the liquid droplets are present in the gas stream assume the stream to be saturated and use a psychrometric chart to obtain an approximation of the moisture percentage.

9.6 Concentration

9.6.1 Calculate the total PCB residue (as DCB) in the sample from the weights of DCB in the perchlorinated aliquots according to Equation A-4.

$$G_s = \frac{5(G_1 + G_2 + G_3)}{3}$$ Equation A-4

9.6.2 Concentration of PCBs (as DCB) in stack gas. Determine the concentration of PCBs in the stack gas according to Equation A-5.

$$C_s = K \frac{G_s}{V_{m(std)}}$$ Equation A-5

where $K = 35.31\ ft^3/m^3$

9.7 Isokinetic variation

9.7.1 Calculations from raw data.

$$I = \frac{100\ T_s\ [K\ V_{lc} + (V_m/T_m)\ (P_{bar} + \Delta H/13.6)]}{60\ \theta\ v_s\ P_s\ A_n}$$

Equation A-6

where $K = 0.00346$ mm Hg-m^3/ml-°K for metric units

$= 0.00267$ in. Hg-ft^3/ml-°R for English units

9.7.2 Calculations from intermediate values.

$$I = \frac{T_s\ V_{m(std)}\ P_{std}\ 100}{T_{std}\ v_s\ \theta\ A_n\ P_s\ 60\ (1-B_{ws})}$$

$$= K \frac{T_s\ V_{m(std)}}{P_s\ v_s\ A_n\ \theta\ (1-B_{ws})}$$ Equation A-7

where $K = 4.323$ for metric units

$= 0.0944$ for English units

9.8 Acceptable results. The following range sets the limit on acceptable isokinetic sampling results:

If 90% < I < 110%, the results are acceptable. If the results are low in comparison to the standards and I is beyond the acceptable range, the Administrator may option to accept the results.

10. Special Cases

10.1 Sampling moisture saturated or supersaturated stack gases. One or two additional modified Greenburg-Smith impingers may be added to the train between the third impinger and the Florisil tube to accommodate additional water collection when sampling high moisture gases. Throughout the preparation, operation, and sample recovery from the train, these additional impingers should be treated exactly like the third impinger.

10.2 PCB verification. It is recommended that an unperchlorinated aliquot from at least one sample be subjected to GC/MS examination to verify that PCB isomers are present.

To accomplish this, the unperchlorinated portion of each extract is first screened by GC with the same chromatographic system used for DCB determination except for a cooler column temperature, typically 165 to 200°C. The elution patterns are compared with those of commercial PCB mixtures (in hexane solution) to determine the most similar mixture.

After determining what PCB isomers are possible present, the sample is examined by GC/MS using multiple ion selection techniques for ions characteristic of the molecular clusters of the PCBs possibly present.

10.3 Evaporation of extracts for perchlorination. For cases where the extract will not evaporate to dryness or excessive PCB loss by volatilization is suspected, the hexane may be removed by azeotrophic evaporation from the hexane/chloroform mixture.

Add 3 ml of chloroform to the aliquot in the culture tube. Add a boiling chip and concentrate by slow boiling in a water bath to 1 ml. Repeat the chloroform addition and evaporation three times in order to remove all residual hexane. Then further concentrate (slowly) to a volume of approximately 0.1 ml. Under no circumstances should the water bath temperature be permitted to exceed 76°C or the solvent be evaporated to dryness. The final volume (0.1 ml) may be determined with sufficient accuracy by comparison of solvent level with another reaction vial containing 0.1 ml of chloroform. When a volume of 0.1 ml is achieved, cap the reaction vial immediately and allow to cool. Proceed with the perchlorination as described in Section 7.3.3.

11. References

Martin, Robert M., "Construction Details of Isokinetic Source Sampling Equipment," Environmental Protection Agency, Air Pollution Control Office Publication No. APTD-0581.

1973 Annual Book of ASTM Standards, Part 23, Designation: D 1179-72.

Thompson, J. F., Ed., "Analysis of Pesticide Residues in Human and Environmental Samples," Environmental Protection Agency, Research Triangle Park, N.C., 1974.

PART B. CAPACITOR- AND TRANSFORMER-FILLING PLANTS

1. Principle and Applicability

1.1 Principle. Gaseous and particulate PCBs are withdrawn isokinetically from the source. The PCBs are collected on Florisil and determined by gas chromatography against an Aroclor® standard.

1.2 Applicability. This method is applicable for the determination of PCB emissions from the room air, room air exhaust and process point exhausts at capacitor- and transformer-filling plants.

2. Range and Sensitivity

The range of the analytical method may be expanded considerably through concentration and/or dilution of the extract. The total method sensitivity is also highly dependent on the volume of gases sampled. However, sensitivity of the total method is near 1 µg per test or near 10 ng per test where the perchlorination assay method is used.

3. Interferences

Throughout all stages of sample handling and analysis, care should be taken to avoid contact of samples and extracts with synthetic organic materials other than TFE® (polytetrafluoroethylene). Lubricating and sealing greases should not be used on the sample exposed portions of the sampling train.

4. Precision and Accuracy

Sampling with identical and paired sampling trains, the precision of the method should be 10 to 15% of the PCB concentration measured. Recovery efficiencies on source samples spiked with PCB compounds ranged from 85 to 95% of the spike.

5. Apparatus

5.1 Sampling Train. The sampling train, see Figure B-1, consists of a glass-lined probe, an adsorbent tube containing Florisil, and the appropriate valving and flow meter controls for isokinetic sampling as described in Part A of the procedure. The sampling apparatus in Figure B-1 is the same as that in Figure A-1 and Section 5.1 of Part A, except that the Smith-Greenburg impingers and heated probe are not used. If condensation of significant quantities of moisture prior to the solid adsorbent is expected, Part A of the method should be used. Since probes and adsorbent tubes are not cleaned up in the field, a sufficient number must be provided for sampling and allowance for breakage.

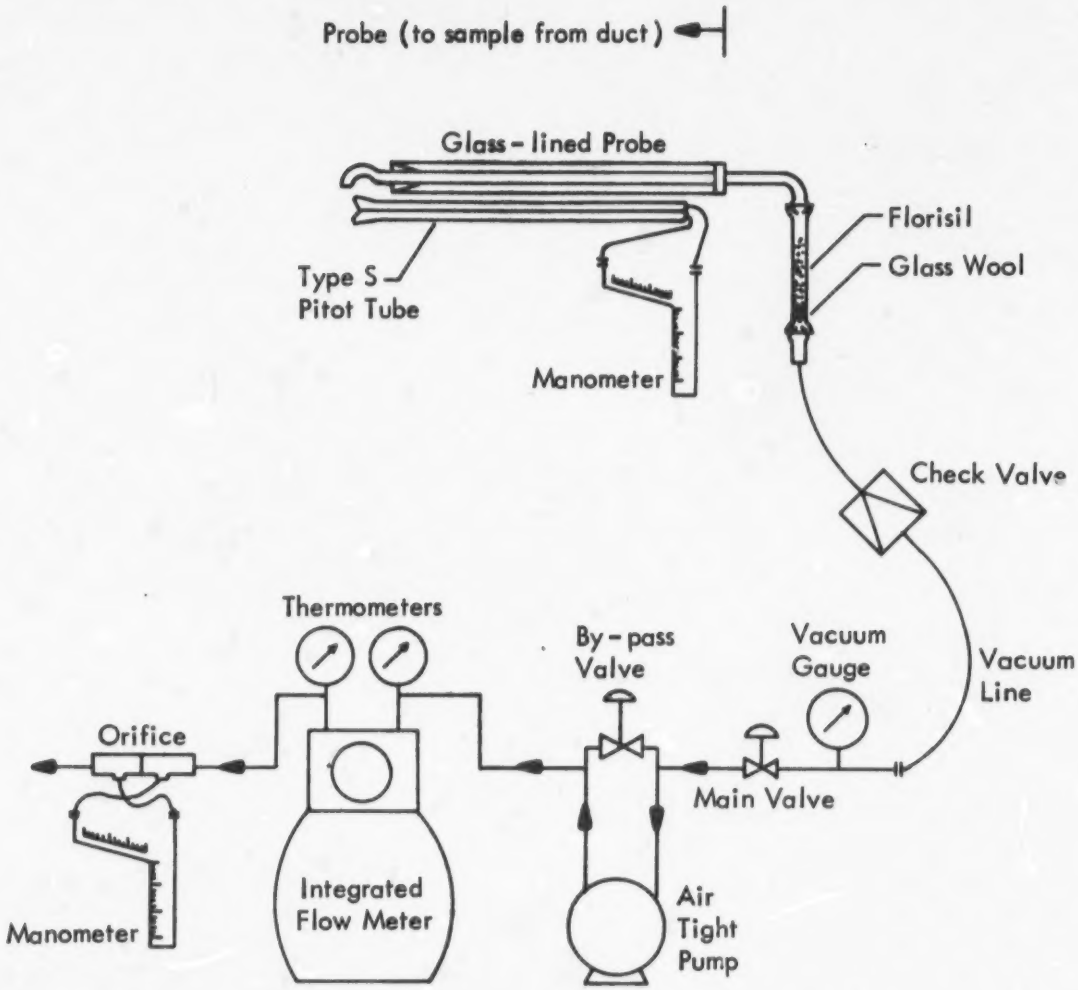

Figure B-1. PCB Sampling Train for Capacitor- and Transformer-Filling Plants

5.2 Sample Recovery. Heavy duty aluminum foil must be provided to cap off the probe prior to shipment.

5.3 Analysis. The equipment required for the analysis is identical to that specified in Part A except that the equipment necessary for perchlorination of the PCBs collected to the decachlorobiphenyl form is not required. (Perchlorination of the sample here is optional and should be employed only if the GC fingerprint technique of this procedure is not applicable.)

6. Reagents

6.1 Sampling

6.1.1 Florisil--Floridin Company, 30/60 mesh, Grade A. The Florisil is cleaned by overnight Soxhlet extraction with hexane and then drying overnight at 110°C and is activated by heating to 650°C for 2 hr (not to exceed 3 hr) in a muffle furnace. After allowing to cool to near 110°C, transfer the clean, active Florisil to a clean, hexane-washed glass jar and seal with a TFE®-lined lid. The Florisil should be stored at 110°C until taken to the field for use. Florisil that has been stored more than 1 month must be reactivated.

6.1.2 Glass wool--Cleaned by thorough rinsing with hexane, dried in a 110°C oven, and stored in a hexane-washed glass jar with TFE®-lined screw cap.

6.2 Analysis

6.2.1 Hexane--Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.2.2 Acetone--Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.2.3 Sodium sulfate (Na_2SO_4)--Anhydrous, granular. Clean by overnight Soxhlet extraction with hexane, drying in a 110°C oven, and then heating to 650°C for 2 hr. Store in 110°C oven or in glass jar closed with TFE®-lined screw cap.

6.2.4 Sulfuric acid (H_2SO_4)--Concentrated, ACS reagent grade or equivalent.

6.2.5 Glass wool--Cleaned by thorough rinsing with hexane, dried in a 110°C oven, and stored in a hexane-rinsed glass jar with TFE®-lined cap.

6.2.6 Carborundum boiling stones--Hengar Company No. 133-B or equivalent, rinsed with hexane.

6.2.7 Standard Aroclor PCB mixtures--Aroclors® 1016, 1221, 1232, 1242, 1248, 1254, 1260, and 1262 may be obtained from the Pesticide Repository, EPA/HERL/ETD, Research Triangle Park, North Carolina.

7. Procedure

7.1 Sampling. The sampling shall be conducted by competent personnel knowledgeable with this test procedure and cognizant of the constraints of the analytical techniques for PCBs, particularly contamination problems.

The sampling procedure for capacitor and transformer plants is identical to that described in Part A with the following exceptions: (a) impingers and a heatable probe are not required prior to the adsorbent tube; and (b) the PCB concentrations may be considerably higher for capacitor and transformer plants, compared to most incinerators, thus the sampling time can be less than the 2 hr specified in Part A.

The selection of sampling time and rate should be based on the approximate levels of PCB residues expected in the sample. The sampling rate should not exceed 14 liters/min and may typically fall in the range of 5 to 10 liters/min. Sampling times should be more than 20 min but should not exceed 4 hr.

Because the processes for filling the capacitors and transformers can vary significantly between plants, isokinetic sampling is required in the procedure. However, if it can be shown to the satisfaction of the Administrator that isokinetic sampling is not necessary, then sampling at a proportional rate is an acceptable alternative. Proportional or constant flow rate sampling may also be necessary in cases where the standard pitot/nozzle assembly physically blocks a significant portion of the stack or where the flow rate is too low (less than 10 ft/min) for the pitot tube.

7.2 Sample Recovery

7.2.1 Adsorbent tube--Remove the Florisil tube from the collection system and cap it off with ground glass caps for shipment to the analytical laboratory.

7.2.2 Probe (where applicable)--Remove the probe from the collection system and cap it off with aluminum foil.

7.3 Analysis. The analysis of the PCB samples should be conducted by chemical personnel experienced in determinations of trace organics utilizing sophisticated instrumental techniques. All extract transfers should be made quantitatively by rinsing the apparatus at least three times with hexane and adding the rinses to the receiving container. A boiling stone should be used in all evaporative steps to control "bumping."

7.3.1 Extraction

7.3.1.1 Adsorbent tube. Expel the entire contents of the adsorbent tube directly onto a glass wool plug in the sample holder of a Soxhlet extractor. Although no extraction thimble is required, a glass thimble with a coarse-fritted bottom may be used.

Rinse the tube with about 5 ml acetone and then about 15 ml hexane into the extractor. Assemble the extraction apparatus and extract the adsorbent with 170 ml hexane for at least 4 hr. The extractor should cycle 10 to 14 times per hour. After allowing the extraction apparatus to cool to ambient temperature, transfer the extract into a Kuderna-Danish evaporator.

Evaporate the extract on a steam bath to about 5 ml and allow the evaporator to cool to ambient temperature before disassembly. Transfer the extract to a 50 ml separatory funnel and set the funnel aside.

7.3.1.2 Probe (where applicable). Rinse the probe with hexane into a Kuderna-Danish evaporator. Evaporate the extract to about 5 ml and allow the evaporator to cool to ambient temperature before disassembly. Add the concentrated extract to the 50-ml separatory funnel containing the corresponding Florisil extract.

7.3.2 Extract cleanup--Clean the combined extracts (in 50-ml separatory funnel) by shaking with 5 ml concentrated sulfuric acid. Allow the acid layer to separate and drain it off.

Transfer the hexane layer to a Kuderna-Danish evaporator and evaporate to about 5 ml. Allow the evaporator to cool to ambient temperature before disassembly.

The extract should be essentially colorless. If it still shows significant color, additional cleanup may be required before assaying for PCBs. In this event, further clean the extract by liquid chromatography on Florisil according to procedures described in Section 5A of the 1974 issue of "Manual of Analytical Methods for Analysis of Pesticide Residues in Human and Environmental Samples." Reduce the Florisil eluant to about 10 ml by Kuderna-Danish evaporation techniques described above.

Transfer the cleaned extract to a 25-ml volumetric flask and dilute to volume with hexane for gas chromatographic analysis.

7.3.3 PCB determination--Assay the cleaned extracts by gas chromatographic comparison with standard solutions of a similar commercial PCB mixture (A column temperature between 165 and 200°C at a flow rate of 30 ml/min may be appropriate. Aroclor® standard solutions at concentrations near 10 ng/µl should be appropriate for calibration of the gas chromatograph.) If PCB mixtures were being used at the sampling site, a standard solution of that mixture, e.g., Aroclor® 1016, will likely be appropriate. Quantitation should be based on the summed areas of at least five major peaks coincident in the chromatograms of the sample extracts and standards. The range and sensitivity of the method may be extended somewhat by diluting concentrated extracts with hexane or concentrating dilute extracts by evaporation under a gentle stream of dry nitrogen. If the sample chromatograms do not closely resemble a particular PCB standard, e.g., in the case of emissions from more than one Aroclor® product, refer to Section 10.1 concerning Special Cases. Correct the PCB assays for PCBs determined in the blank train.

8. Calibration

Maintain a laboratory log of all calibrations.

8.1 Sampling Train

8.1.1 Probe nozzle--Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make three separate measurements using different diameters each time and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.).

When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use.

Each nozzle shall be permanently and uniquely identified.

8.1.2 Pitot tube--The pitot tube shall be calibrated according to the procedure outlined in Method 2.

8.1.3 Dry gas meter and orifice meter--Both meters shall be calibrated according to the procedure outlined in APTD-0576. When diaphragm pumps with bypass valves are used, check for proper metering system design by calibrating the dry gas meter at an additional flow rate of 0.0057 m^3/min (0.2 cfm) with the bypass valve fully opened and then with it fully closed. If there is more than $\pm$ 2% difference in flow rates when compared to the fully closed position of the bypass valve, the system is not designed properly and must be corrected.

8.1.4 Temperature gauges--Calibrate dial and liquid filled bulb thermometers against mercury-in-glass thermometers. Thermocouples need not be calibrated. For other devices, check with the Administrator.

8.2 Analytical Apparatus

8.2.1 Gas chromatograph--Prepare a working curve from at least five standard injections of different volumes of the Aroclor® standard in hexane solution.

9. Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

9.1 Nomenclature

G_s = Total weight of Aroclor® in sample, µg.

C_s = Concentration of Aroclor® in stack gas, $\mu g/m^3$, corrected to standard conditions of 20°C, 760 mm Hg (68°F, 29.92 in. Hg).

A_n = Cross-sectional area of nozzle, m^2 (ft^2).

I = Percent of isokinetic sampling.

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in Hg).

R = Ideal gas constant, 0.06236 mm Hg-m^3/°K-g-mole (21.83 in. Hg-ft^3/°R-lb-mole).

T_m = Absolute average dry gas meter temperature °K (°R).

T_s = Absolute average stack gas temperature °K (°R).

T_{std} = Standard absolute temperature, 293°K (528°R).

V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter corrected to standard conditions, dscm (dscf).

V_s = Stack gas velocity, calculated by Method 2, Equation 2 to 7, m/sec (ft/sec).

ΔH = Average pressure differential across the orifice meter, mm H_2O (in. H_2O).

θ = Total sampling time, min.

13.6 = Specific gravity of mercury.

60 = Sec/min.

100 = Conversion to percent.

9.2 Average dry gas meter temperature and average orifice pressure drop.

9.3 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions [20°C, 760 mm Hg (68°F, 29.92 in. Hg)] by using Equation B-1.

$$V_{m(std)} = V_m \frac{T_{std}}{T_m} \left[\frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}} \right] = KV_m \frac{P_{bar} + \frac{\Delta H}{13.6}}{T_m}$$

Equation B-1

where K = 0.3855 °K/mm Hg for metric units
= 17.65 °R/in. Hg for English units

9.4 Concentration

9.4.1 Concentration of Aroclor® in stack gas. Determine the concentration of Aroclor® in the stack gas according to Equation B-2.

$$C_s = \frac{G_s}{V_{m(std)}}$$

Equation B-2